

**Family list****7** family members for:**GB1364952**

Derived from 7 applications.

- 1 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **BE787762 A1** - 1973-02-19
- 2 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **CH581168 A5** - 1976-10-29
- 3 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **DE2141987 A1** - 1973-02-22
- 4 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **GB1364952 A** - 1974-08-29
- 5 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **IT964112 B** - 1974-01-21
- 6 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **JP48030733 A** - 1973-04-23
- 7 BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS**  
Publication info: **NL7211340 A** - 1973-02-23

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# PATENT SPECIFICATION

(11) 1 364 952

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- (21) Application No. 38657/72 (22) Filed 18 Aug. 1972  
 (31) Convention Application No. P 21 41 987.4  
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 (33) Germany (DT)  
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(19)

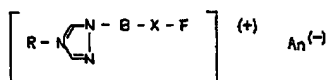


(72) Inventors MANFRED WIESEL and GERHARD WOLFRUM

## (54) BASIC AZO DYESTUFFS CONTAINING TRIAZOLIUM GROUPS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organized under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to valuable new dyestuffs which are free of sulphonic acid groups and carboxylic acid groups, of the general formula

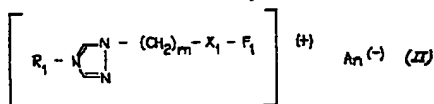


wherein

R denotes an alkyl, alkenyl or aralkyl radical,  
 B denotes a direct bond or a bridge member,  
 X denotes a divalent group,  
 F denotes the radical of an azo-dyestuff and  
 An<sup>-</sup> denotes an anion.

Further subjects of the invention are the manufacture of the new dyestuffs and their use for dyeing and printing natural and synthetic materials, and the materials dyed and printed with these dyestuffs.

The preferred subject of the invention are azo dyestuffs of the general formula



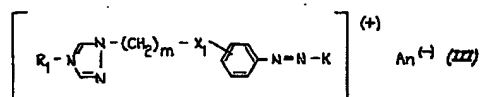
wherein

R<sub>1</sub> denotes an alkyl group with 1 to 4 C atoms or a phenylalkyl group with 1 or 2 C atoms in the alkyl chain,  
 X<sub>1</sub> denotes a —SO<sub>2</sub>—, —NH—SO<sub>2</sub>—, —N(alkyl with 1 to 4 C atoms)—SO<sub>2</sub>—, —CO—, —NH—CO—, —N(alkyl with 1 to 4 C atoms)—CO—, —O—, —S—, —NH—, —N(alkyl with 1 to 4 C atoms), —O—CO— or a direct bond, if m > 1,  
 F<sub>1</sub> denotes the radical of an azo dyestuff,  
 m denotes the numbers 0 to 6 and  
 An<sup>-</sup> denotes an anion,

and wherein

the cyclic and acyclic radicals can be substituted by non-ionic radicals.

Amongst these dyestuffs there should be singled out those of the general formula



wherein

$R_1$  and  $X_1$  are as defined above,

$K$  denotes the radical of a coupling component of the aniline, phenol, naphthylamine, naphthol, indole, pyrazole, pyridine or pyrimidine series,

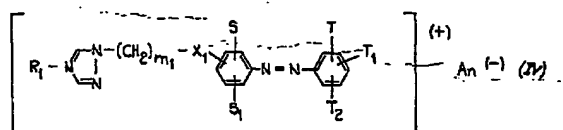
$m$  denotes the numbers 0 to 6 and

$\text{An}^{(-)}$  denotes an anion,

and wherein

the cyclic and acyclic radicals can be substituted by non-ionic radicals.

Particularly preferred dyestuffs are those of the general formula



wherein

$R_1$  and  $X_1$  are as defined above,

$S$  denotes hydrogen, a  $C_1$  to  $C_4$ -alkyl radical, halogen, nitro, methylsulphonyl,  $C_1$  to  $C_4$ -alkoxy,  $C_1$  to  $C_4$ -alkoxycarbonyl or cyano,

$S_1$  denotes hydrogen or halogen,

$T$  denotes hydroxyl or an amino,  $C_1$  to  $C_4$ -dialkylamino,

$C_1$  to  $C_4$ -alkylphenylamino,  $C_1$  to  $C_4$ -alkyl-benzylamino, pyrrolidino, morpholino or piperidino radical,

$T_1$  denotes hydrogen, halogen or a  $C_1$  to  $C_4$ -alkyl,  $C_1$  to  $C_4$ -alkylcarbonylamino or benzoylamino radical,

$T_2$  denotes hydrogen or a  $C_1$  to  $C_4$ -alkoxy radical, or

$T_1$  and  $T_2$  together with the phenyl ring denote a naphthyl radical,

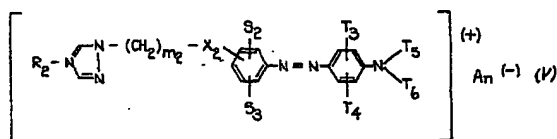
$m_1$  denotes the numbers 0 to 3 and

$\text{An}^{(-)}$  denotes an anion,

and wherein

the cyclic and acyclic radicals can be substituted by non-ionic radicals.

Amongst these dyestuffs there should particularly be singled out those of the general formula



wherein

$R_2$  denotes methyl, ethyl or benzyl,

$X_2$  denotes a  $-\text{SO}_2-$ ,  $-\text{NH}-\text{SO}_2-$ ,  $-\text{N}(\text{CH}_3)-\text{SO}_2-$ ,  $-\text{CO}-$ ,  $-\text{NH}-\text{CO}-$ ,  $-\text{O}-$ ,  $-\text{NH}-$  or  $-\text{O}-\text{CO}-$  group,

$S_2$  denotes hydrogen, chlorine, cyano, methyl, trifluoromethyl or methoxy,

$S_3$  denotes hydrogen or chlorine,

$T_3$  denotes hydrogen or methoxy,

$T_4$  denotes hydrogen, methyl, chlorine, or acetylamino,

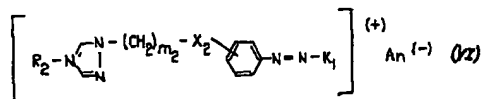
$T_5$  denotes methyl, ethyl or ethyl substituted by hydroxyl, methoxycarbonyl, chlorine or cyano,

$T_6$  denotes hydrogen, methyl, ethyl, benzyl or ethyl substituted by hydroxyl, methoxycarbonyl, chlorine or cyano,

$m_2$  denotes the numbers 1, 2 or 3 and

$\text{An}^{(-)}$  denotes an anion.

Further preferred dyestuffs possess the general formula

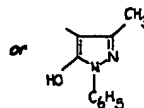
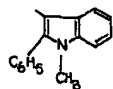


wherein

$R_2$  and  $X_2$  are as defined above,  
 $K_1$  denotes a radical of the formulae

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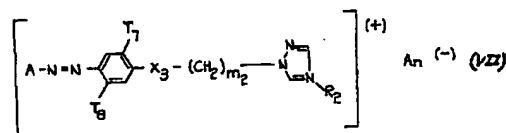
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$m_2$  denotes the numbers, 1, 2 or 3 and  
 $\text{An}^{(-)}$  denotes an anion.

Further preferred dyestuffs are those of the general formula

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wherein

$A$  denotes the radical of a diazo component,  
 $R_2$  denotes methyl, ethyl or benzyl,  
 $T_7$  denotes hydrogen, chlorine or a  $C_1$  to  $C_4$ -alkyl or -alkoxy radical,  
 $T_8$  denotes hydrogen, chlorine, methyl, ethyl, acetyl-amino or, together with the phenyl ring, a naphthyl radical,  
 $X_3$  denotes  $NH-$  or  $-N(C_1 \text{ to } C_4\text{-alkyl})-$ ,  
 $m_2$  denotes the numbers 1, 2 or 3 and  
 $\text{An}^{(-)}$  denotes an anion.

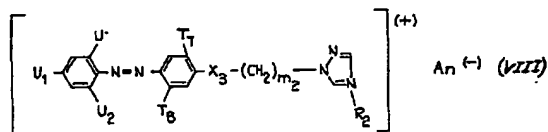
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Amongst these dyestuffs there should be singled out those of the general formula

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wherein

$R_2$ ,  $T_7$ ,  $T_8$ ,  $X_3$  and  $m_2$  are as defined above,  
 $U$  denotes hydrogen, chlorine, bromine, trifluoromethyl, cyano, methyl, methoxy, ethoxy, methoxycarbonyl, ethoxycarbonyl, methylsulphonyl or nitro,  
 $U_1$  denotes hydrogen, chlorine, bromine, cyano, nitro, formyl, methylsulphonyl,  
 $C_1$  to  $C_4$ -alkyl,  $C_1$  to  $C_4$ -alkoxy,  $C_1$  to  $C_4$ -alkoxycarbonyl, phenoxy,  $C_1$  to  $C_4$ -mono- or dialkyl-aminocarbonyl,  $C_1$  to  $C_4$ -mono- or dialkylamino-sulphonyl or phenylazo,  
 $U_2$  denotes hydrogen, chlorine, bromine, trifluoromethyl, cyano, nitro, methyl, hydroxyl, methoxy, ethoxy, methoxycarbonyl or ethoxycarbonyl,  
 and  
 $\text{An}^{(-)}$  denotes an anion.

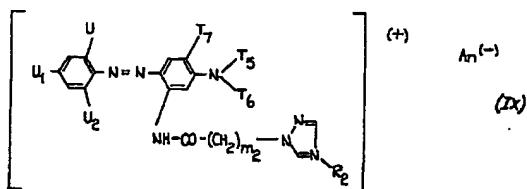
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Further preferred dyestuffs are those of the general formula



wherein

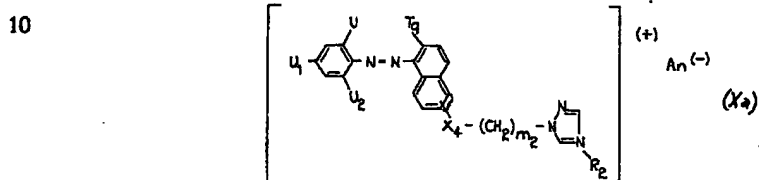
$R_2$ ,  $T_7$ ,  $U$ ,  $U_1$ ,  $U_2$  and  $m_2$  are as defined above,

$T_5$  denotes methyl, ethyl or ethyl substituted by hydroxyl, methoxycarbonyl, chlorine or cyano,

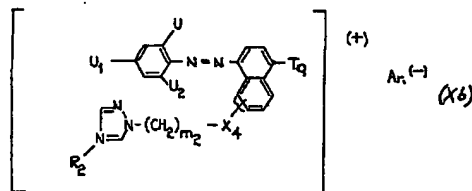
$T_6$  denotes hydrogen, methyl, ethyl, benzyl or ethyl substituted by hydroxyl, methoxycarbonyl, chlorine or cyano,

$\text{An}^{(-)}$  denotes an anion.

Further particularly preferred dyestuffs are those of the general formulae



and



wherein

$R_2$ ,  $U$ ,  $U_1$ ,  $U_2$  and  $m_2$  are as defined above,

$T_8$  denotes  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NH}(\text{C}_1 \text{ to } \text{C}_4\text{-alkyl})$ ,  $-\text{NH}-\text{C}_6\text{H}_5$ ,  $-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_5$  or  $-\text{N}(\text{C}_1 \text{ to } \text{C}_4\text{-alkyl})_2$ ,

$X_4$  denotes  $-\text{CO}-$ ,  $-\text{CO}-\text{O}-$ ,  $-\text{SO}_2-\text{NH}-$  or  $-\text{SO}_2-\text{N}(\text{C}_1 \text{ to } \text{C}_4\text{-alkyl})-$ ,

$\text{An}^{(-)}$  denotes an anion.

Non-ionic substituents in the sense of the present invention are substituents which do not form ionic radicals under the reaction condition under which the dyestuffs are prepared e.g. fluorine, chlorine and bromine; alkyl groups, especially straight-chain or branched alkyl radicals with 1 to 6 C atoms; aralkyl radicals; alkenyl radicals; aryl radicals; alkoxy radicals, especially alkoxy radicals with 1 to 4 C atoms; aralkoxy radicals; aryloxy radicals, alkylthio radicals, preferably alkylthio radicals with 1-3 C atoms; aralkylthio radicals; arylthio radicals; nitro; cyano; alkoxy-carbonyl, preferably those with an alkoxy radical with 1-4 C atoms; the formyl radical; alkylcarbonyl radicals, especially those with an alkyl group with 1-4 C atoms; arylcarbonyl; aralkylcarbonyl radicals; alkoxy-carbonyloxy radicals, preferably with an alkyl group with 1-4 C atoms; alkylcarbonylamino radicals; preferably with an alkyl group with 1-4 C atoms, arylcarbonylamino radicals; alkylsulphonyl-amino radicals, preferably with an alkyl group with 1-3 C atoms; arylsulphonyl-amino groups; ureido; N-aryl- or N-alkyl-ureido, aryloxy-carbonylamino and alkoxy-carbonylamino; carbamoyl; N-alkyl-carbamoyl; N,N-dialkylcarbamoyl; N-alkyl-N-aryl-carbamoyl; sulphamoyl; N-alkylsulphamoyl; N,N-dialkyl-sulphamoyl; alkylsulphonyl; alkenylsulphonyl; aralkylsulphonyl, with 1-4 C atoms being preferably present in the alkyl radicals mentioned; arylsulphonyl, carboxylic acid alkyl ester,

carboxylic acid aryl ether, sulphonic acid alkyl ester and sulphonic acid aryl ester groups.

By an alkyl and alkenyl radicals there are understood a branched or unbranched, aliphatic hydrocarbon radicals with 1—6 C atoms in the case of the alkyl radical and 3—6 C atoms in the case of the alkenyl radicals, which can contain non-ionic substituents and/or carboxyl groups, for example the methyl, ethyl, n- and isopropyl, n-, iso- and tert.-butyl and the various isomeric pentyl and hexyl radicals, as well as the vinyl, allyl or propenyl radical.

Possible anionic radicals  $An^-$  are the organic and inorganic anions which are customary for cationic dyestuffs.

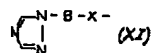
Inorganic anions are, for example, fluoride, chloride, bromide and iodide, perchlorate, hydroxyl, and radicals of acids containing S, such as bisulphate, sulphate, pyrosulphate and sulphamate; radicals of nitrogen-oxygen acids, such as nitrate; radicals of oxygen acids of phosphorus, such as dihydrogen-phosphate, hydrogen-phosphate, phosphate and metaphosphate; radicals of carbonic acid, such as bicarbonate and carbonate; further anions of oxygen acids and complex acids, such as methosulphate, ethosulphate, hexafluosilicate, cyanate, thiocyanate, ferrocyanide, ferricyanide, trichlorozincate and tetrachlorozincate, tribromozincate and tetrabromozincate, stannate, borate, divanadate, tetravanadate, molybdate, tungstate, chromate, bichromate and tetrafluoborate, as well as anions of esters of boric acid, such as of the glycerine ester of boric acid, and of esters of phosphoric acid, such as of methylphosphate.

Organic anions are, for example, anions of saturated or unsaturated aliphatic, cycloaliphatic, aromatic and heterocyclic carboxylic acids and sulphonic acids, such as radicals of acetic acid, chloroacetic acid, cyanoacetic acid, hydroxyacetic acid, aminoacetic acid, methylaminoacetic acid, aminoethyl-sulphonic acid, methylamino-ethyl-sulphonic acid, propionic acid, n-butyric acid, i-butyric acid, 2-methyl-butyric acid, 2-ethyl-butyric acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, 2-chloropropionic acid, 3-chloropropionic acid, 2-chlorobutyric acid, 2-hydroxy-propionic acid, 3-hydroxypropionic acid, O-ethylglycollic acid, thioglycollic acid, glyceric acid, malic acid,  $\omega$ -O-dodecyl- $\omega'$ -O-( $\beta$ -carboxyethyl)-tetraethylene glycol, 3-(nonyloxy) propionic acid, 3-(isotridecyloxy)-propionic acid,  $\omega$ -O-tridecyl- $\omega'$ -O-( $\beta$ -carboxy-ethyl)-diethylene glycol, ethers of 3-hydroxy-propionic acid with mixtures of alcohols with 6 to 10 carbon atoms, thioacetic acid, 6-benzoylamino-2-chlorocaproic acid,  $\omega$ -O-nonylphenyl- $\omega'$ -O-( $\beta$ -carboxyethyl)-tetraethylene glycol and diethylene glycol, phenoxyacetic acid, nonylphenoxyacetic acid, n-valeric acid, i-valeric acid, 2,2,2-trimethylacetic acid, n-caproic acid, 2-ethyl-n-caproic acid, stearic acid, oleic acid, ricinoleic acid, palmitic acid, n-pelargonic acid, lauric acid, a mixture of aliphatic carboxylic acids with 9 to 11 carbon atoms ("Versatic" Acid 911 of SHELL), a mixture of aliphatic carboxylic acids with 15 to 19 carbon atoms ("Versatic" Acid 1519 of SHELL), coconut fatty acid first runnings, undecanecarboxylic acid, n-tridecanecarboxylic acid and a coconut fatty acid mixture; acrylic acid, methacrylic acid, crotonic acid, propargylic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, the isomer mixture of 2,2,4- and 2,4,4-trimethyladipic acid, sebacic acid, isosebacic acid (isomer mixture), tartaric acid, citric acid, glyoxylic acid, dimethyl-ether- $\alpha,\alpha'$ -dicarboxylic acid, methylene-bis-thioglycollic acid, dimethylsulphide- $\alpha,\alpha'$ -dicarboxylic acid, 2,2'-dithio-di-n-propionic acid, fumaric acid, maleic acid, itaconic acid, ethylene-bis-amino-acetic acid, methanesulphonic acid, ethanesulphonic acid, chloromethanesulphonic acid, 2-chloroethanesulphonic acid and 2-hydroxyethanesulphonic acid and mersolate, that is to say  $C_n-C_{13}$  paraffinsulphonic acid obtained by chlorosulphonation of paraffin oil.

Suitable anions of cycloaliphatic carboxylic acids are, for example, the anions of cyclohexanecarboxylic acid and cyclohexene-3-carboxylic acid, and anions of araliphatic monocarboxylic acids are, for example, anions of phenylacetic acid, 4-methylphenylacetic acid and mandelic acid.

Suitable anions of aromatic carboxylic acids are, for example, the anions of benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, 4-tert-butylbenzoic acid, 2-bromobenzoic acid, 2-chlorobenzoic acid, 3-chlorobenzoic acid, 4-chlorobenzoic acid, 2,4-dichlorobenzoic acid, 2,5-dichlorobenzoic acid, 2-nitrobenzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 2-chloro-4-nitrobenzoic acid, 6-chloro-3-nitrobenzoic acid, 2,4-dinitrobenzoic acid, 3,4-dinitrobenzoic acid, 3,5-dinitrobenzoic acid, 2-hydroxybenzoic acid, 3-hydroxybenzoic acid, 4-hydroxybenzoic acid, 2-mercaptobenzoic acid, 4-nitro-3-methylbenzoic acid, 4-aminobenzoic acid, 5-nitro-2-hydroxybenzoic acid, 3-nitro-2-hydroxybenzoic acid, 4-methoxybenzoic acid, 3-nitro-4-methoxybenzoic acid, 4-chloro-3-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, 5-chloro-2-hydroxy-3-methyl-

- benzoic acid, 4-ethylmercapto-2-chlorobenzoic acid, 2-hydroxy-3-methylbenzoic acid, 6-hydroxy-3-methylbenzoic acid, 2-hydroxy-4-methylbenzoic acid, 6-hydroxy-2,4-dimethylbenzoic acid, 6-hydroxy-3-tert-butylbenzoic acid, phthalic acid, tetrachlorophthalic acid, 4-hydroxyphthalic acid, 4-methoxyphthalic acid, isophthalic acid, 4-chloroisophthalic acid, 5-nitro-isophthalic acid, terephthalic acid, nitroterephthalic acid and diphenyl-3,4-carboxylic acid, *o*-vanillic acid, 3-sulphobenzoic acid, benzene-1,2,4,5-tetracarboxylic acid, naphthalene-1,4,5,8-tetracarboxylic acid, biphenyl-4-carboxylic acid, abietic acid, phthalic acid mono-*n*-butyl ester, terephthalic acid monoethyl ester, 3-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, 2-hydroxy-1-naphthoic acid and anthraquinone-2-carboxylic acid.
- Suitable anions of heterocyclic carboxylic acids are, for example, the anions of pyromucic acid, dehydromucic acid and indolyl-3-acetic acid.
- Suitable anions of aromatic sulphonic acids are, for example, the anions of benzenesulphonic acid, benzene-1,3-disulphonic acid, 4-chlorobenzenesulphonic acid, 3-nitrobenzenesulphonic acid, 6-chloro-3-nitrobenzenesulphonic acid, toluene-4-sulphonic acid, toluene-2-sulphonic acid, toluene-*m*-sulphonic acid, 2-chlorotoluene-4-sulphonic acid, 1-hydroxybenzenesulphonic acid, *n*-dodecylbenzenesulphonic acid, 1,2,3,4-tetrahydronaphthalene-6-sulphonic acid, naphthalene-1-sulphonic acid, naphthalene-1,4- or -1,5-disulphonic acid, naphthalene-1,3,5-trisulphonic acid, 1-naphthol-2-sulphonic acid, 5-nitronaphthalene-2-sulphonic acid, 8-aminonaphthalene-1-sulphonic acid, stilbene-2,2'-disulphonic acid and biphenyl-2-sulphonic acid.
- A suitable anion of heterocyclic sulphonic acids is, for example, the anion of quinoline-5-sulphonic acid.
- Further possibilities are the anions of arylsulphinic, -phosphonic and -phosphonous acids, such as benzenesulphinic acid and benzenephosphonic acid.
- Colourless anions are preferred. For dyeing from an aqueous medium, anions which do not excessively impair the solubility of the dyestuff in water are preferred. For dyeing from organic solvents, anions which assist the solubility of the dyestuff in organic solvents or at least do not influence it negatively are also preferred.
- The anion is generally determined by the manufacturing process and by the purification of the crude dyestuff which may be carried out. In general, the dyestuffs are in the form of halides (especially chlorides or bromides) or methosulphates, ethosulphates, sulphates, benzenesulphonates or toluenesulphonates, or acetates. The anions can be replaced by other anions in a known manner.
- The new dyestuffs of the formula I are obtained if, in accordance with methods which are in themselves known, either a grouping of the general formula



wherein

- B and X have the meaning indicated in the formula I, is introduced by known methods into an azo dyestuff or into an amino or azo coupling component, which is diazotised and coupled with a coupling component or coupled with a diazotised amine, respectively, and the resulting dyestuff is subsequently quaternised with a compound of the general formula



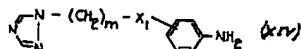
XII

- wherein
- R has the meaning indicated in the formula I and
- An<sub>1</sub> represents a radical which can split off under the reaction conditions as an anion and can be identical with An or is replaceable by An,
- or a grouping of the general formula

- An<sup>(-)</sup>  $\left[ \text{R} - \text{N} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{array} \text{B-X-} \right]^{(+)} \quad (\text{XIII})$

is introduced by known methods into an azo dyestuff or into an amine or azo coupling component, which is subsequently diazotised and coupled with a coupling component or coupled with a diazotised amine, respectively. Thus, azo dyestuffs of the formula III can be manufactured by diazotising amines of the general formula





coupling the product with compounds of the general formula



XV

and subsequently quaternising with compounds of the general formula

5



XVI

5

In the formulae XIV to XVI,

$\text{R}_1$ ,  $\text{K}$ ,  $\text{X}_1$  and  $m$  have the meaning indicated in the formula III and

$\text{An}_1$  represents a radical which can split off under the reaction conditions as an anion and which can be identical with  $\text{An}$  or replaceable by  $\text{An}$ .

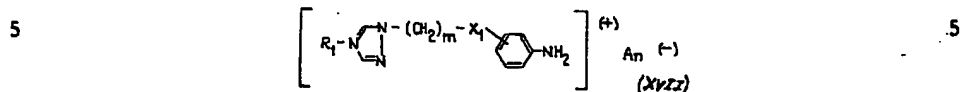
- 10 Suitable amines XIV are, for example: 4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 4-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butylamide, 3-chloro-4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-amide, 3-chloro-4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-amino-4-chloro-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-chloro-4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-amino-4-chloro-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-chloro-4-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-amino-4-chloro-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 2-amino-3-chloro-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-chloro-4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butylamide, 3-chloro-4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl-methylamide, 3-amino-4-chloro-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl-methylamide, 2,5-dichloro-4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-amide, 2,5-dichloro-4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 2,5-dichloro-4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methyl-methylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-methylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-ethylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl-methylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl-ethylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl-methylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl-ethylamide, 2,5-dichloro-4-amino-benzenesulphonic acid  $\omega$ -[(1,2,4-triazolyl)-(1)]-hexylamide, 2-amino-5-methyl-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 2-amino-5-methyl-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 2-amino-5-methyl-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-methylamide, 2-amino-4-methyl-5-chloro-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 2-amino-4-methyl-5-chloro-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-methylamide, 2-amino-4-methyl-5-chloro-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-ethylamide, 2-amino-4-methyl-5-chloro-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-methyl-4-amino-benzenesulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-methyl-4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-methyl-4-amino-benzenesulphonic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-methylamide, 3-methyl-4-amino-benzenesulphonic acid  $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, [(1,2,4-triazolyl)-(1)]-methyl-(4-aminophenyl)-sulphone, [(1,2,4-triazolyl)-(1)]-methyl-(3-aminophenyl)-sulphone, [(1,2,4-triazolyl)-(1)]-methyl-(2-aminophenyl)-sulphone,  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-(4-aminophenyl)-sulphone,  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-(3-aminophenyl)-sulphone,  $\gamma$ -

	[(1,2,4-triazolyl)-(1)]-propyl-(4-aminophenyl)-sulphone, $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl-(3-aminophenyl)-sulphone, $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl-(4-aminophenyl)-sulphone, [(1,2,4-triazolyl)-(1)]-methyl-(3-chloro-4-aminophenyl)-sulphone, $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-(3-chloro-4-aminophenyl)-sulphone, $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl-(3-chloro-4-aminophenyl)-sulphone, [(1,2,4-triazolyl)-(1)]-methyl-(3-amino-4-chlorophenyl)-sulphone, $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-(3-amino-4-chlorophenyl)-sulphone, $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl-(3-amino-4-chlorophenyl)-sulphone, [(1,2,4-triazolyl)-(1)]-methyl-(2,5-dichloro-4-aminophenyl)-sulphone, $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-(2,5-dichloro-4-aminophenyl)-sulphone, $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl-(2,5-dichloro-4-aminophenyl)-sulphone, $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl-(2,5-dichloro-4-aminophenyl)-sulphone, 3-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-ethylamide, 3-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 4-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-methylamide, 4-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-ethylamide, 4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 4-amino-benzoic acid $\omega$ -[(1,2,4-triazolyl)-(1)]-butylamide, 3-chloro-4-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-chloro-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-chloro-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-chloro-4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-chloro-4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-methyl-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-methyl-4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 2,5-dimethyl-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 2,5-dimethyl-4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-methoxy-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-methoxy-4-amino-benzoic acid $\gamma$ -[(1,2,4-triazolyl)-(1)]-propylamide, 3-methoxy-4-amino-benzoic acid $\omega$ -[(1,2,4-triazolyl)-(1)]-butylamide, 3-trifluoromethyl-4-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-trifluoromethyl-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-nitro-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-nitro-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, 3-cyano-4-amino-benzoic acid [(1,2,4-triazolyl)-(1)]-methylamide, 3-cyano-4-amino-benzoic acid $\beta$ -[(1,2,4-triazolyl)-(1)]-ethylamide, [(1,2,4-triazolyl)-acetic acid 4-aminoanilide, [(1,2,4-triazolyl)-(1)]-acetic acid 3-aminoanilide, [(1,2,4-triazolyl)-(1)]-acetic acid 3-chloro-4-aminoanilide, [(1,2,4-triazolyl)-(1)]-acetic acid N-methyl-(4-aminoanilide), [(1,2,4-triazolyl)-(1)]-acetic acid N-methyl-(3-aminoanilide), [(1,2,4-triazolyl)-(1)]-acetic acid N-methyl-(3-chloro-4-aminoanilide), [(1,2,4-triazolyl)-(1)]-acetic acid N-methyl-(4-amino-3-chloroanilide), $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 4-aminoanilide, $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 3-aminoanilide, $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 3-chloro-4-aminoanilide, $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 3-amino-4-chloroanilide, $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid N-methyl-(4-aminoanilide), $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid N-methyl-(3-aminoanilide), $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid N-methyl-(3-chloro-4-aminoanilide), $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid N-methyl-(3-amino-4-chloroanilide), $\omega$ -[(1,2,4-triazolyl)-(1)]-butyric acid 3-amino-4-chloroanilide, N-[(1,2,4-triazolyl)-(1)]-methyl-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-chloro-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-nitro-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-nitro-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-chloro-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-methyl-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-nitro-4-amino-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-trifluoromethylaniline, N-[(1,2,4-triazolyl)-(1)]-methyl-3-amino-4-methylsulphonyl-aniline, N-[(1,2,4-triazolyl)-(1)]-propyl-3-amino-4-chloro-aniline, [(1,2,4-triazolyl)-(1)]-methyl 4-aminophenyl ketone, [(1,2,4-triazolyl)-(1)]-methyl-3-amino-4-chlorophenyl ketone, $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl 4-aminophenyl ketone, $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl-3-chloro-4-aminophenyl ketone, $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl 3-amino-4-nitro-phenyl ketone, $\gamma$ -[(1,2,4-triazolyl)-(1)]-	
5		5
10		10
15		15
20		20
25		25
30		30
35		35
40		40
45		45
50		50
55		55
60		60
65		65

- propyl 4 - aminophenyl ketone,  $\gamma$  - [(1,2,4 - triazolyl) - (1)] - propyl 3 - chloro-4-aminophenyl ketone,  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl 3-nitro-4-aminophenyl ketone, 4-amino-benzoic acid  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl ester, 4-amino-benzoic acid  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl ester, 3-chloro-4-amino-benzoic acid  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl ester, 3-chloro-4-amino-benzoic acid  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl ester, 4-chloro-3-amino-benzoic acid  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl ester, 4-chloro-3-amino-benzoic acid  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl ester, 3-methyl-4-amino-benzoic acid  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl ester, 3-methyl-4-amino-benzoic acid  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl ester,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 4-aminophenyl ether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 3-aminophenyl ether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 3-chloro-4-aminophenyl ether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 3-nitro-4-aminophenyl ether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 3-methylsulphonyl-4-aminophenyl ether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 3-amino-4-bromophenyl ether,  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl 4-aminophenyl ether,  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl 3-cyano-4-aminophenyl ether,  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl 3-amino-4-chlorophenyl ether, [(1,2,4-triazolyl)-(1)]-methyl 4-aminophenyl thioether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 4-aminophenyl thioether,  $\beta$  - [(1,2,4-triazolyl)-(1)]-ethyl 3-amino-4-chlorophenyl thioether,  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl 4-aminophenyl thioether and  $\gamma$  - [(1,2,4-triazolyl)-(1)]-propyl 3-aminophenyl thioether.
- 20 Suitable coupling components XV are, for example: phenol, *m*-cresol, *p*-cresol, 3-chlorophenol, *N,N*-dimethylaniline, *N,N*-dimethyl-*m*-toluidine, *N,N*-diethylaniline, *N,N*-diethyl-*m*-toluidine, *N*-ethyl-*N*- $\beta$ -cyanoethyl-aniline, *N*-ethyl-*N*- $\beta$ -cyanoethyl-*m*-toluidine, *N,N*-bis-( $\beta$ -cyanoethyl)-aniline, *N,N*-bis-( $\beta$ -cyanoethyl)-*m*-toluidine, *N*-ethyl-*N*-( $\beta$ -hydroxyethyl)-aniline, *N*-ethyl-*N*-( $\beta$ -hydroxyethyl)-*m*-toluidine, *N,N*-bis-( $\beta$ -hydroxyethyl)-aniline, *N,N*-bis-( $\beta$ -hydroxy-ethyl)-*m*-toluidine, *N*-ethyl-*N*-benzyl-aniline, *N*-ethyl-*N*-benzyl-*m*-toluidine, *N*-methyl-diphenyl-amine, *N*-ethyl-*N*-( $\beta$ -methoxy-carbonyl-ethyl)-aniline, *N,N*-bis-( $\beta$ -methoxy-carbonyl-ethyl)-aniline, *N*-ethyl-*N*-( $\beta$ -methoxy-carbonyl-ethyl)-*m*-toluidine, *N,N*-bis-( $\beta$ -methoxy-carbonyl-ethyl)-*m*-toluidine, *N,N*-dimethyl-*m*-acetyl-amino-aniline, *N,N*-diethyl-*m*-acetyl-amino-aniline, *N*-ethyl- $\beta$ -hydroxyethyl-*m*-acetyl-amino-aniline, *N*-ethyl-*N*-( $\beta$ -acetoxycarbonyl-ethyl)-*m*-benzoylamino-aniline, *N*-ethyl-*N*-( $\beta$ -benzoyloxyethyl)-*m*-chloroacetyl-amino-aniline, *N*-ethyl-*N*-( $\beta$ -phenoxyethyl)-*m*-hydroxyacetyl-amino-aniline, *N*-ethyl-*N*-( $\beta$ -methoxyethyl)-*m*-chloroacetyl-amino-aniline, *N,N*-diethyl-2-methoxy-5-acetyl-amino-aniline, *N,N*-diethyl-2-ethoxy-5-acetyl-amino-aniline, *N*-ethyl-*N*-( $\beta$ -chloroethyl)-aniline, *N*-ethyl-*N*-( $\beta$ -chloroethyl)-*m*-toluidine, *N*-phenyl-morpholine, 2-methyl-indole, 1,2-dimethyl-indole,
- 35 1-methyl-2-phenyl-indole, 2-ethylindole, 2-phenylindole, 1- $\beta$ -cyanoethyl-2-methylindole, 1- $\beta$ -cyanoethyl-2-phenyl-indole,  $\gamma$ -(2-phenylindolyl-1)-propionic acid amide, 2- $\beta$ -naphthyl-indole, 2-biphenyl-indole, 2,5-dimethylindole, 2-phenyl-5-ethoxy-indole, 2-methyl-5-chloroindole, 2-methyl-6-chloroindole, 2-methyl-5-nitro-indole,  $\alpha$ -naphthol,  $\beta$ -naphthol,  $\alpha$ -naphthylamine, 1-ethyl-1,2,3,4-tetrahydroquinoline, 2,6-dihydroxy-3-cyano-4-methyl-pyridine, 2,4,6-trisethylamino-pyrimidine, 2,4,6-tris-dimethylamino-pyrimidine, 1-phenyl-3-methyl-5-amino-pyrazole, 1-phenyl-3-methyl-5-pyrazolone, 1-(2-chlorophenyl)-3-methyl-5-pyrazolone, 1-(3-chlorophenyl)-3-methyl-5-pyrazolone, 1-(2,5-dichlorophenyl)-3-methyl-5-pyrazolone, 1-(2-nitrophenyl)-3-methyl-5-pyrazolone, 1-(3-nitrophenyl)-3-methyl-5-pyrazolone, 1-(*p*-tolyl)-3-methyl-5-pyrazolone, 1-benzyl-3-methyl-5-pyrazolone, 1-(3-sulpho-lanyl)-3-methyl-5-pyrazolone, 1-phenyl-5-pyrazolone-3-carboxylic acid amide, 1-phenyl-5-pyrazolone-3-carboxylic acid ethyl ester, 1-phenyl-3-methoxycarbonylmethyl-5-pyrazolone, 1- $\beta$ -cyanoethyl-3-methyl-5-pyrazolone, 1- $\beta$ -chloroethyl-3-ethyl-5-pyrazolone and 1- $\beta$ -acetoxycethyl-3-ethyl-5-pyrazolone.
- 50 The coupling takes place in a manner which is in itself known, for example in a neutral, acid or weakly alkaline aqueous medium.
- 55 The quaternisation is appropriately effected by warming in an inert organic solvent, for example in hydrocarbons such as benzene, toluene or xylene, halogenated hydrocarbons, such as carbon tetrachloride, tetrachloroethane, chlorobenzene and *o*-dichlorobenzene, nitro-hydrocarbons, such as nitromethane, nitrobenzene or nitronaphthalene or in dimethylformamide, acetonitrile or dimethylsulphoxide, using preferably equivalent amounts of alkylating agents, for example with methyl chloride, methyl bromide, methyl iodide, ethyl bromide, benzyl chloride, trimethylxonium fluoborate, dimethyl sulphate, diethyl sulphate and *p*-toluenesulphonic acid methyl ester, ethyl ester or butyl ester.
- 60 The resulting quaternised dyestuffs are sparingly soluble in the solvents used and can be isolated by filtering them off. If, when using dimethyl formamide, dimethyl sulphoxide or acetonitrile, the quaternised dyestuffs remain partially or completely in

solution, they can be separated out by dilution with water and adding water-soluble salts, for example sodium chloride or potassium chloride.

A further way to manufacture the azo dyestuffs of the formula III consists in diazotising the amines of the general formula



and coupling with the coupling component XV,  
wherein

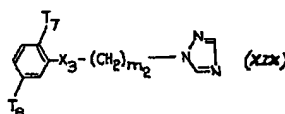
the symbols have the meaning indicated in the formula III.

10 The azo dyestuffs of the formula VII are manufactured if either amines of the general formula

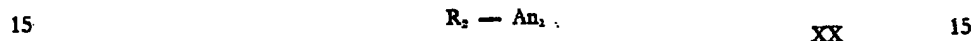


XVIII

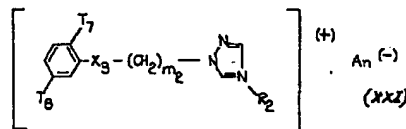
are diazotised and the product is coupled with compounds of the general formula



and subsequently quaternised with compounds of the general formula



or amines XVIII are coupled, after diazotisation, with compounds of the general formula



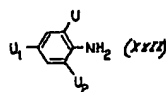
In the formulae XVIII — XXI

20 A, R<sub>1</sub>, T<sub>7</sub>, T<sub>8</sub>, X<sub>2</sub> and m<sub>2</sub> have the meaning indicated in the formula VII and An<sub>1</sub> represents a radical which can be split off as an anion and which can be identical with An or replaceable by An. 20

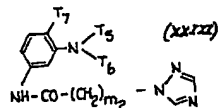
Suitable coupling components XIX are, for example: N-methyl-N-[(1,2,4-triazolyl)-(1)]-methyl-aniline, N-ethyl-N-(β-[(1,2,4-triazolyl)-(1)]-ethyl)-aniline, 25 N-ethyl-N-(γ-[(1,2,4-triazolyl)-(1)]-propyl)-aniline, N-methyl-N-[(1,2,4-triazolyl)-(1)]-methyl-*m*-toluidine, N-ethyl-N-(β-[(1,2,4-triazolyl)-(1)]-ethyl)-*m*-toluidine, N-ethyl-N-(γ-[(1,2,4-triazolyl)-(1)]-propyl)-*m*-toluidine, N-methyl-N-[(1,2,4-triazolyl)-(1)]-methyl-2-methoxy-5-methyl-aniline, N-ethyl-N-(β-[(1,2,4-triazolyl)-(1)]-ethyl)-2-methoxy-5-methyl-aniline, N-ethyl-N-(γ-[(1,2,4-triazolyl)-(1)]-propyl)-2-methoxy-5-methyl-aniline, N-[(1,2,4-triazolyl)-(1)]-methyl-α-naphthylamine and N-(β-[(1,2,4-triazolyl)-(1)]-ethyl)-α-naphthyl- 30

The dyeing of the dyestuffs according to the invention, of the formulae (I) to amine.

35 The azo dyestuffs of the formula IX are manufactured in that either amines of the general formula 35



are diazotised and the products are coupled with compounds of the general formula

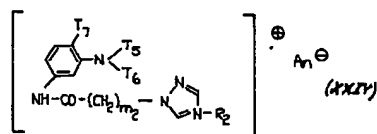


and subsequently quaternised with compounds of the general formula



XX

or amines XXII are coupled, after diazotisation, with compounds of the general formula



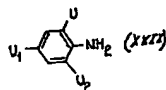
In the formulae XX, XXII, XXIII and XXIV

U, U1, U2, R2, T5, T6, T7 and m2 have the meaning indicated in the formula IX and

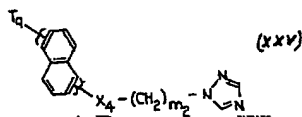
An1 represents a radical which can split off under the reaction conditions as an anion and which can be identical with An or replaceable by An.

Suitable coupling components XXIII are, for example: [(1,2,4-triazolyl)-(1)]-acetic acid 3-dimethylamino-anilide, [(1,2,4-triazolyl)-(1)]-acetic acid 3-dimethylamino-4-methoxy-anilide,  $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 3-dimethylamino-anilide,  $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 3-dimethylamino-4-methoxy-anilide, [(1,2,4-triazolyl)-(1)]-acetic acid 3-diethylamino-anilide, [(1,2,4-triazolyl)-(1)]-acetic acid 3-diethylamino-4-methoxy-anilide and  $\beta$ -[(1,2,4-triazolyl)-(1)]-propionic acid 3-diethylamino-anilide.

The azo dyestuffs of the formulae Xa and Xb are manufactured in that either amines of the general formula



are diazotised and the products are coupled with compounds of the general formula

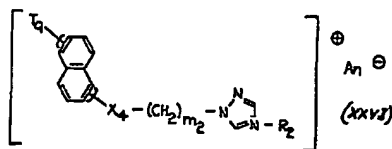


and subsequently quaternised with compounds of the general formula



XX

or amines XXII are coupled, after diazotisation, with compounds of the general formula



In the formulae XX, XXII, XXV and XXVI,

U, U<sub>1</sub>, U<sub>2</sub>, T<sub>1</sub>, X<sub>1</sub>, m<sub>1</sub> and R<sub>1</sub> have the meaning indicated in the formulae Xa or Xb and

An<sub>1</sub> represents a radical which can be split off as an anion and which can be identical with An or replaceable by An.

Suitable coupling components XXV are, for example:  $\beta$ -aminonaphthalene-5-sulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide,  $\beta$ -aminonaphthalene-5-sulphonic acid ( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide,  $\beta$ -aminonaphthalene-5-sulphonic acid ( $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl)-amide,  $\beta$ -aminonaphthalene-5-sulphonic acid ( $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl)-amide,  $\beta$ -aminonaphthalene-6-sulphonic acid [(1,2,4-triazolyl)-(1)]-methylamide,  $\beta$ -aminonaphthalene-6-sulphonic acid ( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide,  $\beta$ -aminonaphthalene-6-sulphonic acid ( $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl)-amide,  $\beta$ -aminonaphthalene-6-sulphonic acid ( $\omega$ -[(1,2,4-triazolyl)-(1)]-butyl)-amide,  $\alpha$ -aminonaphthalene-6-sulphonic acid ( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide,  $\alpha$ -aminonaphthalene-6-sulphonic acid ( $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl)-amide,  $\alpha$ -hydroxynaphthalene-6-sulphonic acid ( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide,  $\alpha$ -hydroxynaphthalene-6-sulphonic acid ( $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl)-amide,  $\beta$ -hydroxynaphthalene-6-sulphonic acid ( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide, 2-hydroxy-naphthalenecarboxylic acid 3-( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide and 2-hydroxy-naphthalenecarboxylic acid 3-( $\gamma$ -[(1,2,4-triazolyl)-(1)]-propyl)-amide.

Suitable diazo components XVIII or XXII are, for example: 4-nitroaniline, 2,4-dinitroaniline, 2-chloro-4-nitroaniline, 4-chloro-2-nitroaniline, 2,5-dichloro-4-nitroaniline, 2,6-dichloro-4-nitroaniline, 2-methoxy-4-nitroaniline, 2-cyano-4-nitroaniline, 2-trifluoromethyl-4-chloroaniline, 2-cyano-6-chloro-4-nitroaniline, 2,4-dinitro-6-bromoaniline, 4-cyanoaniline, 3,4-dicyanoaniline, 2-cyano-5-chloroaniline, 4-cyano-3-chloroaniline, 2,4-dicyano-6-chloroaniline, 3-nitro-4-amino-benzoic acid butyl ester, 4-nitro-2,6-dicyanoaniline, 2-chloroaniline, 3-chloroaniline, 4-chloroaniline, 2-nitroaniline, 3-nitroaniline, 2-chloro-3-nitroaniline, 2-chloro-4,6-dinitroaniline, 2-nitro-3-chloroaniline, 2,4-dicyanoaniline, 2,3-dichloroaniline, 3,4-dichloroaniline, 2,4,5-trichloroaniline, pentachloroaniline, 2-chloro-4-methylaniline, 2-methyl-4-chloroaniline, 3-chloro-4-aminobenzoic acid ethyl ester, 4-aminobenzoic acid ethyl ester, 4-aminobenzoic acid methyl ester, 3-nitro-4-aminobenzoic acid ethyl ester, 4-phenylsulphonylaniline, 4-aminobenzoic acid dimethylamide, 4-methylsulphonylaniline, 2-trifluoromethyl-4-methylsulphonylaniline, 4-methoxyaniline, 3-methoxyaniline, 2-nitro-4-methoxyaniline, 2-methoxy-4-nitroaniline, 2-bromo-4-nitroaniline, 3-bromo-4-nitroaniline, 2-bromo-4-cyanoaniline, 3-bromo-4-cyanoaniline, 2-nitro-4-bromoaniline, 3-nitro-4-bromoaniline, 3-cyano-4-bromoaniline, 3-chloro-4-nitroaniline, 3-nitro-4-chloroaniline, 2-trifluoromethylaniline, 2-trifluoromethyl-4-cyanoaniline, 4-trifluoromethylaniline, 2-chloro-4-trifluoromethylaniline, 2-nitro-4-trifluoromethylaniline, 3-chloro-4-trifluoromethylaniline, 3-nitro-4-trifluoromethylaniline, 2,6-dibromotoluidine, 2-methylaniline, 3-methylaniline, 4-methylaniline, 4-aminoazobenzene and 2-amino-4-phenyl-1,3,5-thiadiazole.

The dyestuffs obtained according to the process are outstandingly suitable for dyeing and printing cationically dyeable fibres of polymers and copolymers of acrylonitrile and of dicyanoethylene and of acid-modified fibres of synthetic polyamides and polyesters, giving fast colour shades. The dyestuffs can also be used for dyeing and printing tannin-treated cellulose materials, silk and leather. They are furthermore suitable for the manufacture of writing fluids, rubber-stamp inks and ball pen pastes and can also be used in flexographic printing.

Suitable goods for dyeing with the basic dyestuffs of the general formulae (I) to (X) are especially flocks, fibres, filaments, tapes, woven fabrics or knitted fabrics of polyacrylonitrile or of copolymers, containing at least 85% of acrylonitrile, of acrylonitrile with other vinyl compounds, such as vinyl chloride, vinylidene chloride, vinyl fluoride, vinyl acetate, vinylpyridine, vinylimidazole, vinyl alcohol, acrylic and methacrylic acid esters and amides and asymmetrical dicyanoethylene. Equally, excellent

dyeing of flocks, fibres, filaments, tapes, woven fabrics or knitted fabrics of acid-modified synthetic materials, especially of acid-modified aromatic polyesters and acid-modified polyamide fibres, is possible. Acid-modified aromatic polyesters are, for example, polycondensation products of sulphoterephthalic acid and ethylene glycol, that is to say polyethylene glycol terephthalates containing sulphonic acid groups (grade "DACRON" 64 of E.I. DuPont de Nemours and Company), such as are described in Belgian Patent Specification 549,179 and U.S.A. Patent Specification 2,893,816.

Dyeing is possible from a weakly acid liquor, with the goods appropriately being introduced into the dyebath at 40° to 60°C and then dyed at the boil. Dyeing can also be carried out under pressure at temperatures above 100°C. Furthermore, the dyestuffs can be added to spinning solutions for the manufacture of fibres containing polyacrylonitrile or be applied to the unstretched fibre.

The dyeings of the dyestuffs according to the invention, of the formulae (I) to (X), on materials of polyacrylonitrile or acid-modified polyester fibres or polyamide fibres are distinguished by very good fastness to light, wet processing, rubbing and sublimation and by high affinity to the fibre.

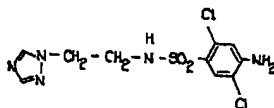
The dyestuffs can be employed individually or as mixtures. They are very suitable for dyeing mouldings of polymers or copolymers of acrylonitrile, asymmetrical dicyanoethylene, acid-modified aromatic polyesters or acid-modified synthetic polyamide in chlorinated hydrocarbons as the dyebath, provided they possess substituents which assist the solubility in chlorinated hydrocarbons, such as, for example, the tert.-butyl group, or provided the anion  $\text{Arr}^-$  in the formulae I to X is the anion of a monobasic organic acid with 4 — 30 carbon atoms.

Such organic acids are, for example: 2-ethylcaproic acid, lauric acid, oleic acid, linoleic acid, a mixture of aliphatic carboxylic acids with 15 — 19 carbon atoms (Versatic Acid 1519), a mixture of aliphatic carboxylic acids with 9 — 11 carbon atoms (Versatic Acid 911), coconut fatty acid first runnings, tetradecanoic acid, undecylenic acid, dimethylpropionic acid, dimethylacetic acid, carboxylic acids of which the carbon chain is interrupted by hetero-atoms, such as  $\omega$ -O-nonylphenyl- $\omega'$ -O-( $\beta$ -carboxyethyl)-tetraethylene glycol,  $\omega$ -O-dodecyl- $\omega'$ -O-( $\beta$ -carboxyethyl)-tetraethylene glycol 3-(nonyloxy)-propionic acid, 3-(isotridecyloxy)-propionic acid, the ethers of 3-hydroxy-propionic acid with mixtures of alcohols with 6 — 10 carbon atoms, nonylphenoxyacetic acid, aromatic carboxylic acids, such as tert.-butylbenzoic acid, cycloaliphatic carboxylic acids, such as hexahydrobenzoic acid, cyclohexenecarboxylic acid, and abietic acid and sulphonic acids, such as tetrapropylenebenzenesulphonic acid.

In the examples which follow, parts denote parts by weight.

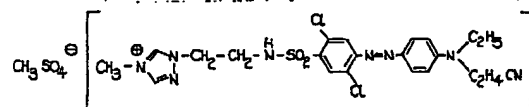
#### Example 1.

A solution of 33.6 parts of 2,5-dichloro-4-amino-benzene-sulphonic acid ( $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl)-amide



in a mixture of 150 parts of water and 30 parts of concentrated hydrochloric acid is diazotised at 0—3°C with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is then added to a solution of 17.4 parts of N-ethyl-N-( $\beta$ -cyanoethyl)-aniline in a mixture of 50 parts of water and 25 parts of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts immediately; it is completed by gradual addition of sodium acetate solution and after completion of coupling and neutralisation with ammonia solution the resulting dyestuff is filtered off. 51 parts of a red dyestuff powder are obtained.

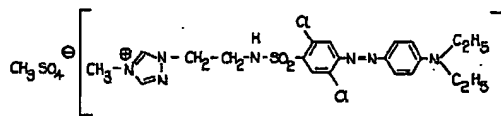
26 parts of this dyestuff are heated to 90° in 200 parts of 1,2-dichlorobenzene and 6.3 parts of dimethyl sulphate are added in portions. The mixture is stirred for a further 2 hours at 100°. After cooling, the dyestuff is filtered off, washed with benzene and dried. 29.2 parts of powder of the formula



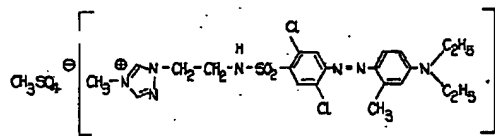
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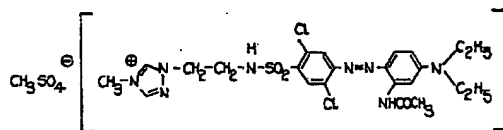
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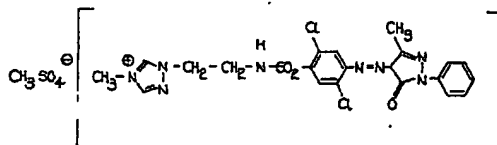
10


$$\text{CH}_3\text{SO}_4^- \left[ \text{CH}_3-\text{N}^+\equiv\text{N}-\text{CH}_2-\text{CH}_2-\text{N}^-\text{SO}_2-\text{C}_6\text{H}_2(\text{Cl})_2-\text{N}=\text{N}-\text{C}_6\text{H}_3(\text{Cl})(\text{CH}_3)-\text{N}^-(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4\text{OH}) \right]$$

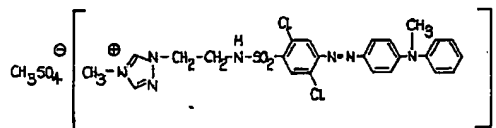
**red**



claret  
red

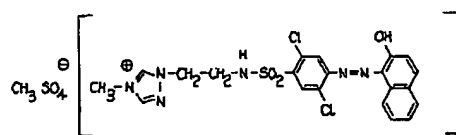
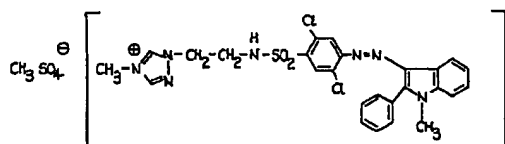
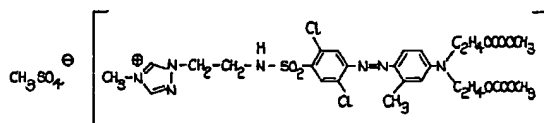


**yellow**

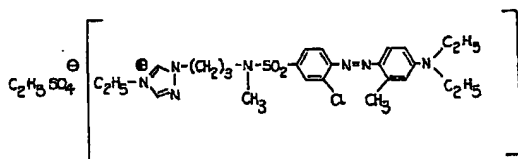


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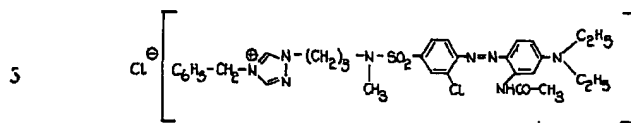


golden  
yellowgolden  
yellow

scarlet

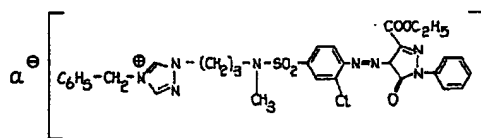


red

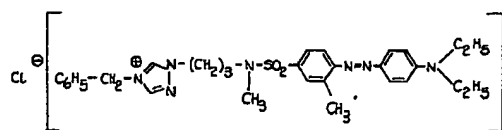


red

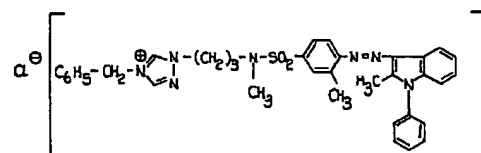
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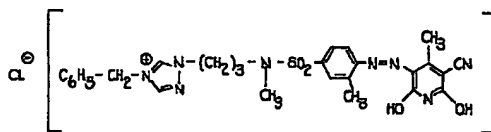
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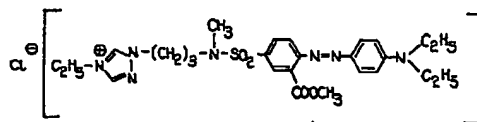
orange



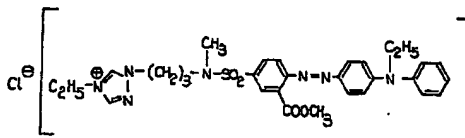
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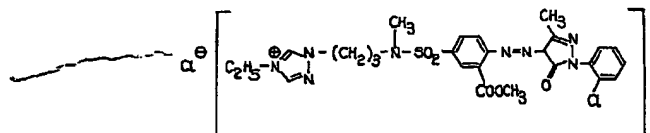
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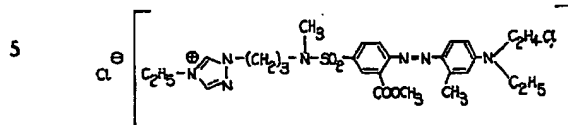
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red

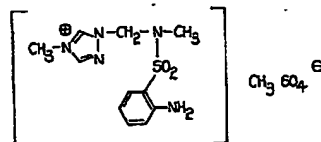


yellow



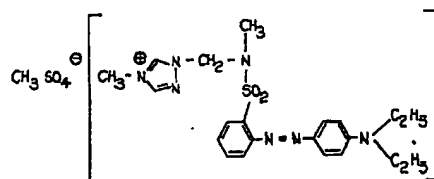
red

Example 2.  
39.3 parts of (2-aminobenzenesulphonic acid [(4-methyl-[(1,2,4-triazolium)-(1)]-methyl]-methyl-amide)-methosulphate



in a mixture of 150 parts of water and 20 parts of concentrated hydrochloric acid are diazotised at 0—3° with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is added to a solution of 14.9 parts of diethylaniline in a mixture of 50 parts of water and 15 parts of concentrated hydrochloric acid.

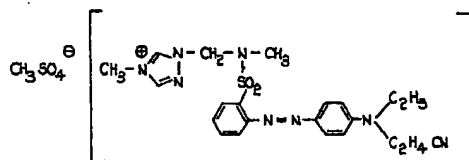
The coupling to give the monoazo dyestuff starts immediately. It is completed by gradual addition of sodium acetate solution. The resulting dyestuff is separated out by adding 30 parts of sodium chloride and is filtered off. The dyestuff has the composition



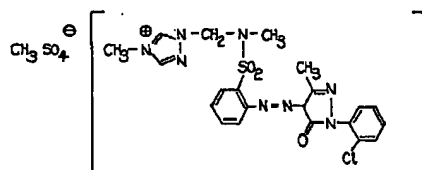
and dyes textile fabrics of polyacrylonitrile, acid-modified polyester and polyamide in an orange-red colour having very good fastness to wet processing and very good fastness to light.

5 The diazo component of this example was manufactured by reaction of 2-nitrobenzenesulphochloride and 1-methyl-amino-methyl-1,2,4-triazole, subsequent quaterni- 5 sation with dimethyl sulphate and final catalytic reduction of the nitro group to the amino group.

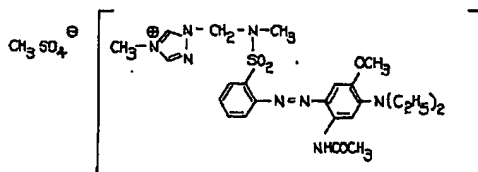
10 With further coupling components these diazo components analogously give the 10 following dyestuffs:



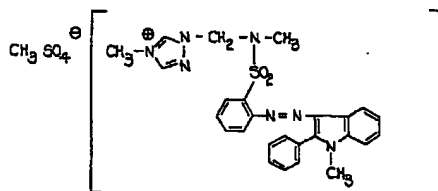
red



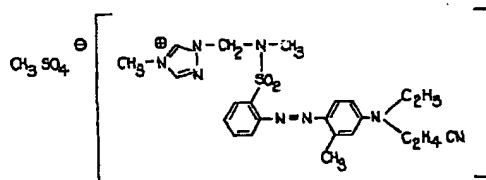
yellow



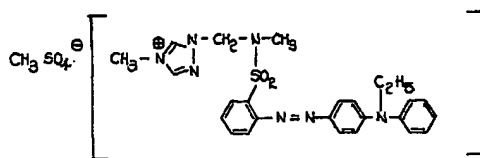
bluish-tinged red



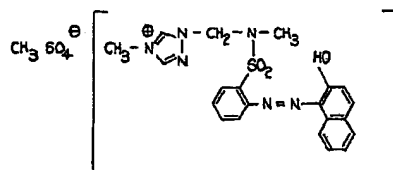
yellow



red



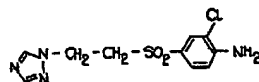
red

golden  
yellow

## Example 3.

5 A solution of 28.7 parts of  $(\beta-[(1,2,4\text{-triazolyl})-(1)]\text{-ethyl})-(3\text{-chloro-4-aminophenyl})\text{-sulphone}$

5



10 in a mixture of 150 parts of water and 30 parts of concentrated hydrochloric acid is diazotised at  $0-3^\circ$  with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is then added to a solution of 17.4 parts of N-ethyl-N-( $\beta$ -cyanoethyl)-aniline in a mixture of 50 parts of water and 25 parts of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts immediately; it is completed by gradual addition of sodium acetate solution and after completion of coupling and neutralisation with ammonia solution the resulting dyestuff is filtered off. 45 parts of a red dyestuff powder are obtained.

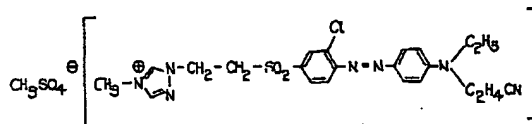
10

15 23.5 parts of this dyestuff in 200 parts of chlorobenzene are warmed to  $90^\circ$  and 6.3 parts of dimethyl sulphate are added in portions. The mixture is stirred for a further 2 hours at  $100^\circ$ . After cooling, the dyestuff is filtered off, washed with benzene and dried. 29 parts of a powder of the formula

15

20

20



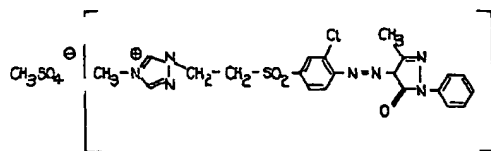
are obtained, which is easily soluble in water to give a red colour and dyes textile materials of polyacrylonitrile and acid-modified polyamide and polyester in a red colour of excellent fastness to light and to wet processing.

25

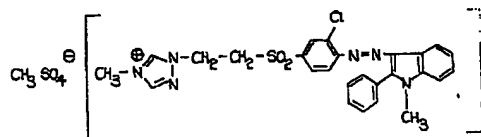
The sulphone used as the diazo component in this example was obtained by reaction of 3-chloro-4-nitro-benzene-sulphinic acid and 1-bromo-2-[(1,2,4-triazole)-(I)]-ethane and subsequent catalytic reduction of the nitro group.

25

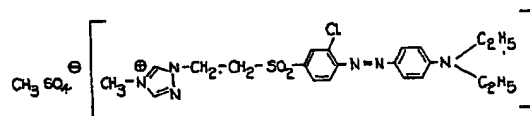
The following dyestuffs are obtained analogously:



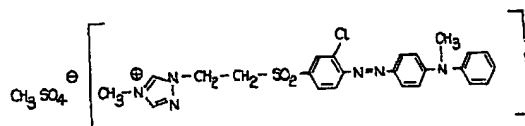
yellow



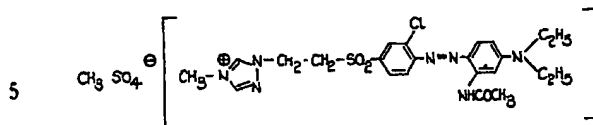
yellow



red

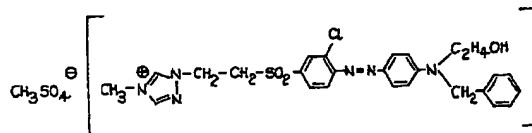


red

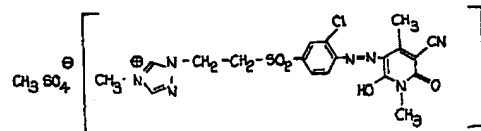


red

5



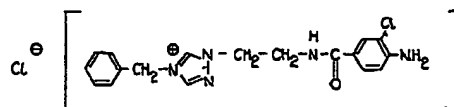
orange



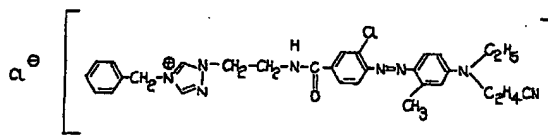
yellow

## Example 4.

A solution of 35.7 parts of 1-( $\beta$ -(3-chloro-4-amino-benzoylamino))-ethyl-4-benzyl-(1,2,4)-triazolium) chloride

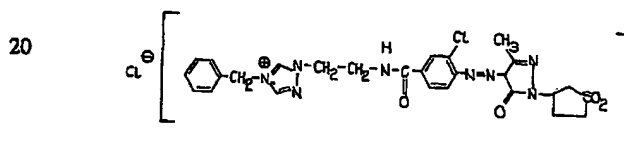


- 5 in a mixture of 150 parts of water and 20 parts of concentrated hydrochloric acid is  
5 diazotised at 0–3°C with a solution of 6.9 parts of sodium nitrite in 50 parts of  
water. The clear diazonium salt solution is freed of a slight excess of nitrous acid  
by means of amidosulphonic acid and is then added to a solution of 18.8 parts of  
10 N-ethyl-N( $\beta$ -cyanoethyl)-*m*-toluidine in a mixture of 50 parts of water and 20 parts  
of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts  
immediately. It is completed by adding sodium acetate solution. The dyestuff is  
separated out by adding 30 parts of sodium chloride and filtered off. The resulting  
dyestuff has the composition



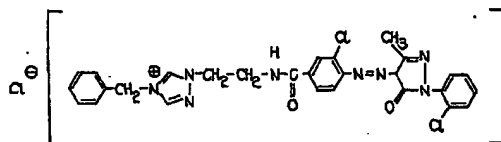
and dyes textile fabrics of polyacrylonitrile, acid-modified polyamide and polyester  
in an orange-red colour having very good wet fastness properties and very good fastness  
to light.

On using further coupling components, the diazo components of Example 5  
analogously gives the following dyestuffs:

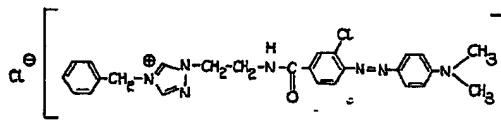


yellow

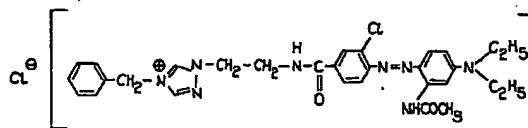
20



yellow



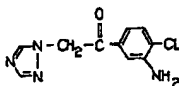
orange



red

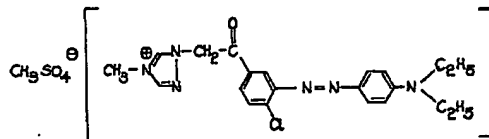


**Example 5.**  
A solution of 25.3 parts of 1-(3-amino-4-chlorobenzoyl-methyl)-1,2,4-triazole



5 in a mixture of 150 parts of water and 50 parts of concentrated hydrochloric acid is diazotised at 0—3°C with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is then added to a solution of 14.9 parts of N,N-diethyl-aniline in a mixture of 50 parts of water and 15 parts of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts immediately; it is completed by gradual addition of sodium acetate solution and after completion of coupling and neutralisation with ammonia solution the resulting dyestuff is filtered off. 39 parts of a red dyestuff powder are obtained.

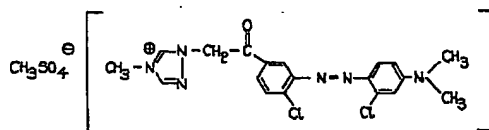
10 20.6 parts of this dyestuff are heated to 100° in 200 parts of chlorobenzene and 6.3 parts of dimethyl sulphate are added in portions. The mixture is stirred for a further 2 hours at 100°C. After cooling, the dyestuff is filtered off, washed with benzene and dried. 25.2 parts of a powder of the formula



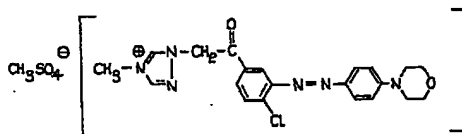
15 are obtained, which is easily soluble in water to give an orange-red colour and dyes textile materials of polyacrylonitrile and acid-modified polyamide and polyester in a yellowish-tinged red colour of excellent fastness to light and to wet processing.

20 The amine used as the diazo component in this example was obtained by reaction of 3-nitro-4-chlorophenyl chloromethyl ketone with 1,2,4-triazole and catalytic reduction.

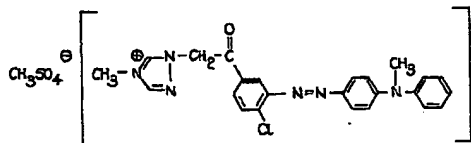
The following dyestuffs are obtained analogously:



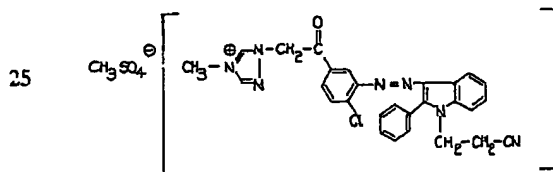
yellow-  
tinged  
orange



yellow-  
tinged  
orange



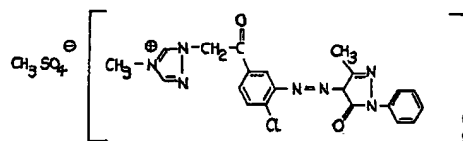
orange



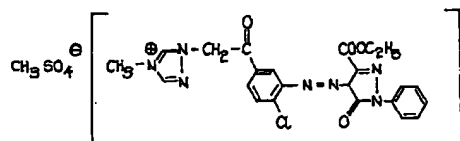
yellow

25

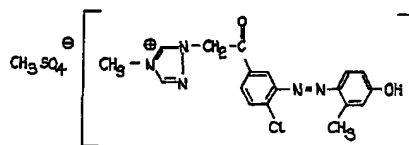




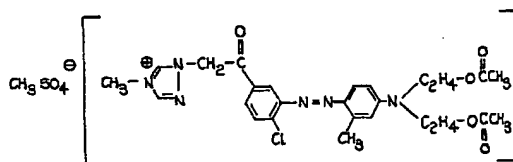
yellow



yellow



orange



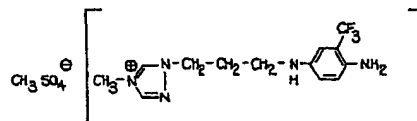
orange

5

## Example 6.

A solution of 26.7 parts of 1-(γ-(3-trifluoromethyl-4-aminophenyl-amino)-propyl)-4-methyl-1,2,4-triazolium-methosulphate

5

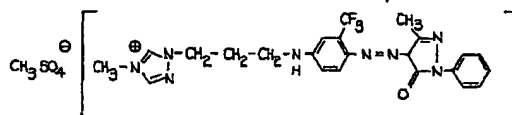


10

in a mixture of 150 parts of water and 30 parts of concentrated hydrochloric acid is diazotised at 0—3° with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is then added to a solution of 17.4 parts of 1-phenyl-3-methyl-5-pyrazolone in a mixture of 100 parts of water, 10 parts of a 40% strength sodium hydroxide solution and 8.4 parts of sodium bicarbonate. The coupling to give the monoazo dyestuff starts immediately and is completed after a short time. The yellow dyestuff is separated out by adding 30 parts of sodium chloride and is filtered off. The resulting dyestuff has the composition

10

15



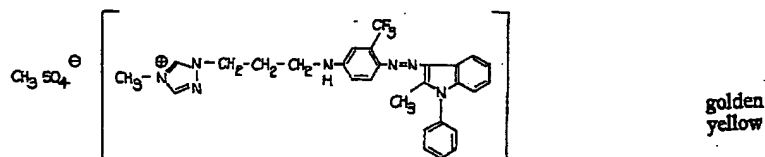
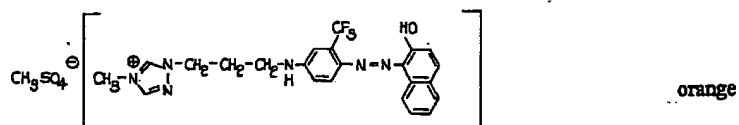
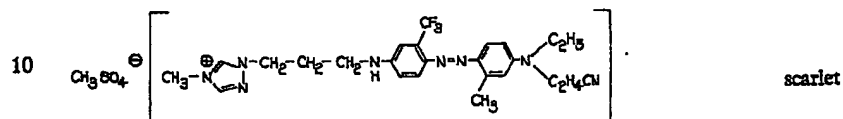
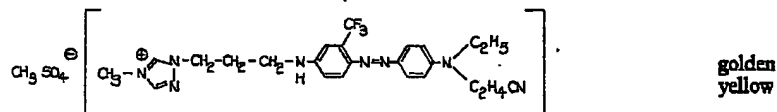
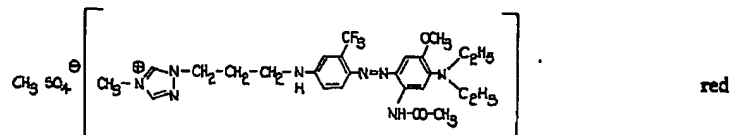
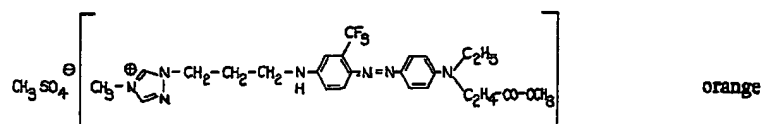
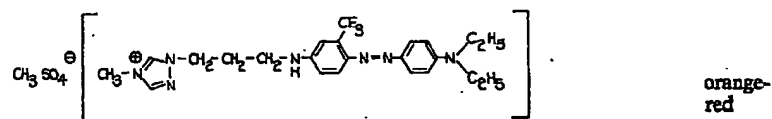
15

and dyes textile fabrics of polyacrylonitrile, acid-modified polyamide and polyester in a yellow colour having very good fastness to wet processing and very good fastness to light.

If further coupling components are used, the diazo component of Example 7 analogously yields the following dyestuffs:

5

5



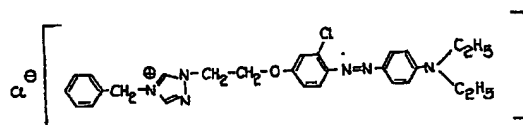


are obtained, which is easily soluble in water to give an orange-red colour and dyes textile materials of polyacrylonitrile and acid-modified polyamide and polyester in a yellowish-tinged red colour of excellent fastness to light and to wet processing.

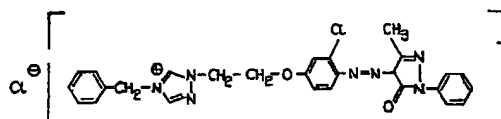
Using further coupling components, the following dyestuffs are obtained analogously:

5

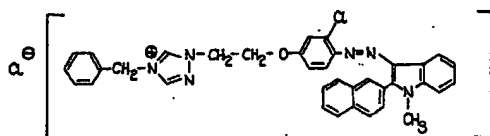
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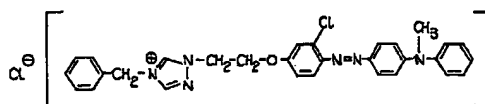
orange



yellow

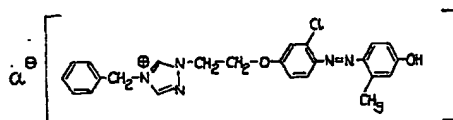


yellow



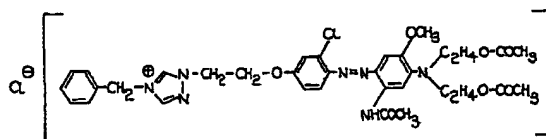
orange

10

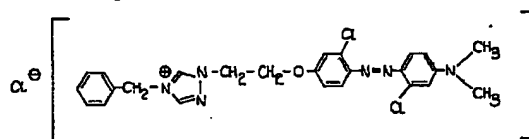


orange

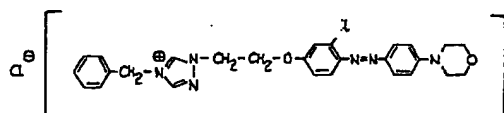
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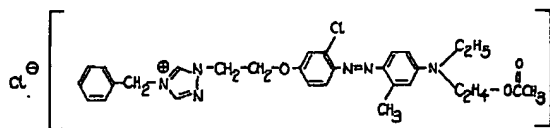
red



yellow-tinged orange



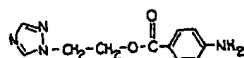
orange



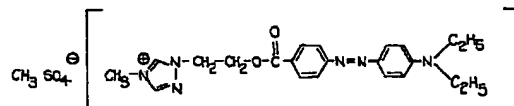
scarier

## Example 8.

A solution of 23.2 parts of 4-aminobenzoic acid  $\beta$ -[(1,2,4-triazolyl)-(1)]-ethyl ester

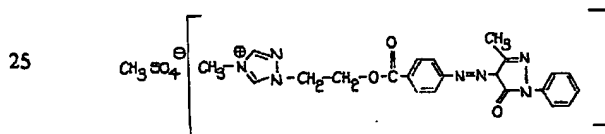


in a mixture of 150 parts of water and 30 parts of concentrated hydrochloric acid is diazotised at 0—3° with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is then added to a solution of 14.9 parts of diethylaniline in a mixture of 50 parts of water and 20 parts of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts immediately; it is completed by gradual addition of sodium acetate solution and after neutralisation with ammonia solution the resulting dyestuff is filtered off. 37.1 parts of a red dyestuff powder are obtained. 19.6 parts of this dyestuff in 200 parts of chlorobenzene are heated to 90° and 6.4 parts of dimethyl sulphate are added in portions. The mixture is stirred for a further 2 hours at 90°. After cooling, the dyestuff is filtered off, washed with benzene and dried. 24.1 parts of a powder of the formula

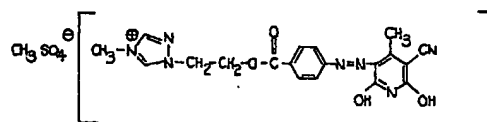


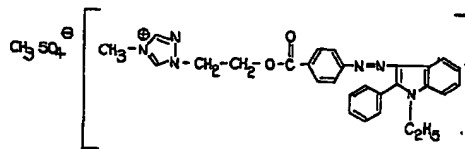
are obtained, which is easily soluble in water to give an orange-red colour and dyes textile materials of polyacrylonitrile and acid-modified polyamide and polyester in an orange colour having excellent fastness to wet processing and to light.

Using further coupling components, the following dyestuffs are obtained analogously:

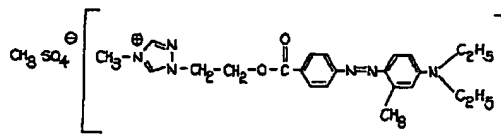


yellow

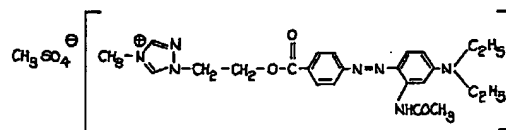




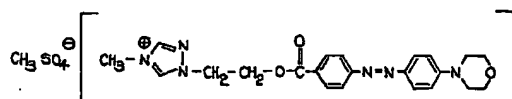
yellow



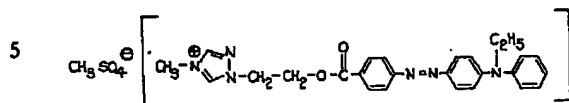
orange



red

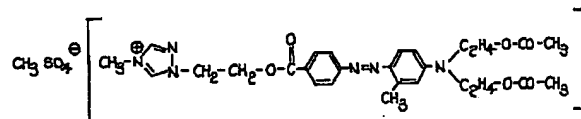


orange



orange

5

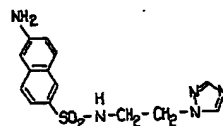


"

## Example 9.

A solution of 13.8 parts of 4-nitroaniline in a mixture of 30 parts of concentrated hydrochloric acid and 250 parts of  $\text{H}_2\text{O}$  is stirred for 1 hour at  $30^\circ$ . After cooling to  $10^\circ$ , 350 parts of ice are added and thereafter the substance is diazotised with 7 parts of sodium nitrite in 70 parts of water. The filtered diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid.

The diazo solution is run, with cooling, into a solution of 31.7 parts of  $\beta$ -aminonaphthalene-6-sulphonic acid  $\beta[(1,2,4\text{-triazolyl})-(1)]$ -ethyl-amide



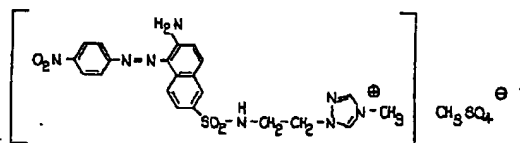
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10

in 400 parts of water and 20 parts of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts immediately; it is completed by gradual addition of sodium acetate solution. After filtration and drying, 43.2 parts of a red dyestuff powder are obtained.

- 5 23.3 parts of this dyestuff are heated to 90° in 200 parts of chlorobenzene and 6.3 parts of dimethyl sulphate are added in portions. The mixture is stirred for a further 2 hours at 100°. After cooling, the dyestuff is filtered off, washed with benzene and dried. 28.5 parts of a powder of the formula

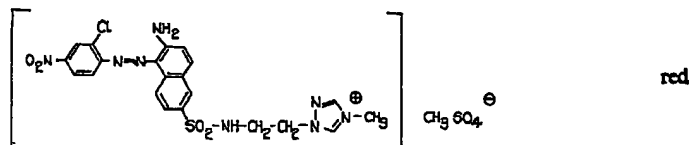
5



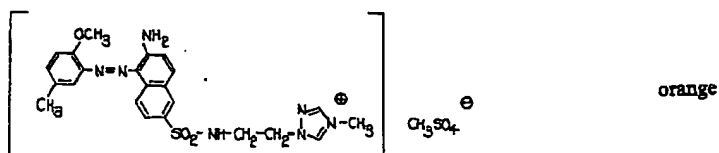
- 10 are obtained, which is easily soluble to give a red colour and dyes textile materials of polyacrylonitrile and acid-modified polyamide and polyester in a red colour of excellent fastness to light and wet processing.

10

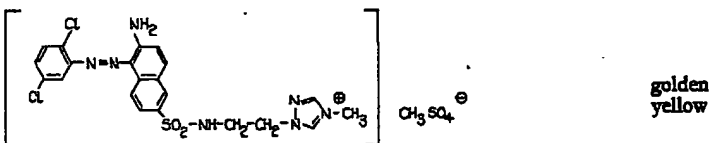
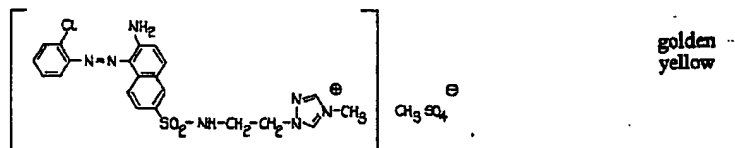
Using further diazo components, the following dyestuffs are obtained analogously:

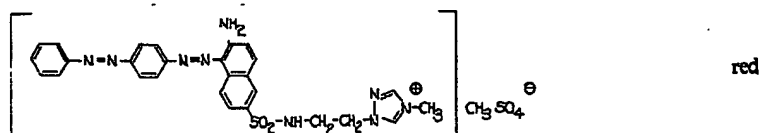
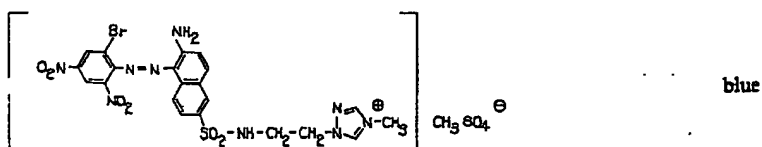
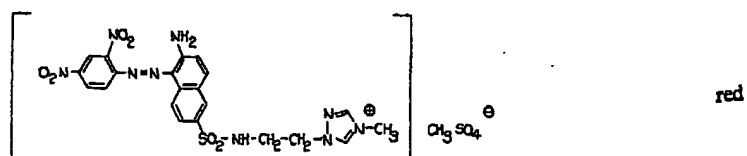
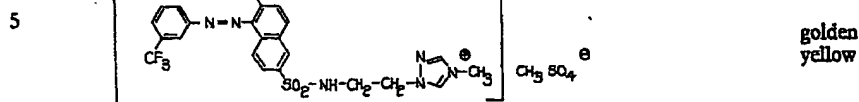
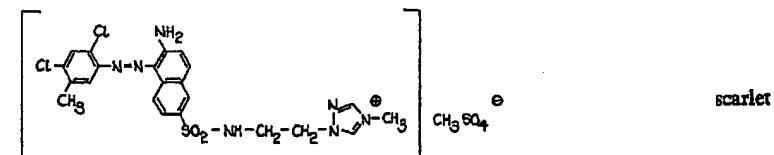
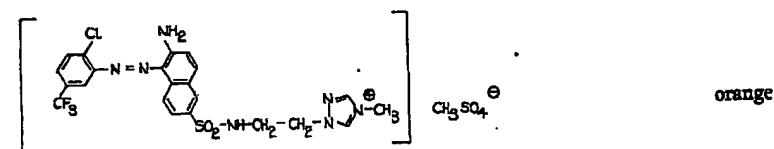
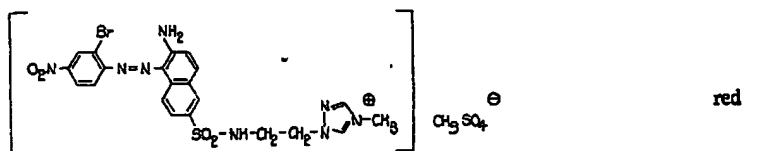
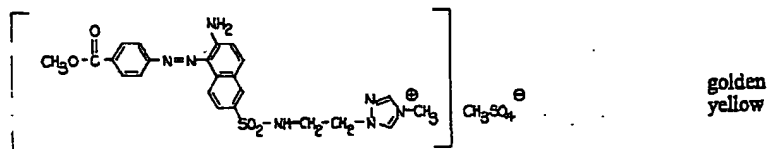


15



15

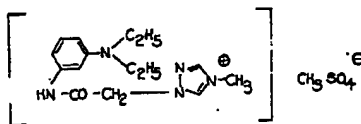




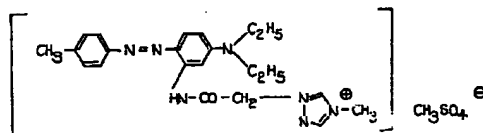


## Example 10

A solution of 10.7 parts of *p*-toluidine in a mixture of 150 parts of water and 30 parts of concentrated hydrochloric acid is diazotised at 0—3° with a solution of 6.9 parts of sodium nitrite in 50 parts of water. The clear diazonium salt solution is freed of a slight excess of nitrous acid by means of amidosulphonic acid and is then added, after cooling, to a solution of 41.5 parts of [4-methyl-1,2,4-triazolium-(1,)]-acetic acid (3-diethyl-aminoanilide) : methosulphate



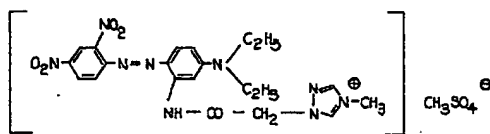
in a mixture of 150 parts of water and 20 parts of concentrated hydrochloric acid. The coupling to give the monoazo dyestuff starts immediately and is completed by gradual addition of sodium acetate solution. The resulting dyestuff is separated out by adding 50 parts of sodium chloride and is filtered off. The dyestuff has the composition



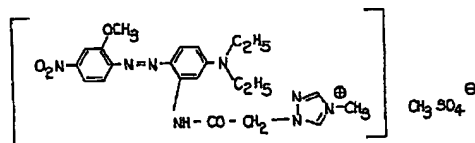
and dyes textile fabrics of polyacrylonitrile, acid-modified polyester and polyamide in an orange colour having very good fastness to wet processing and to light.

The coupling component of this example was manufactured by reaction of chloroacetic acid (3-diethylamino)-anilide with 1,2,4-triazole and subsequent quaternisation with dimethyl sulphate.

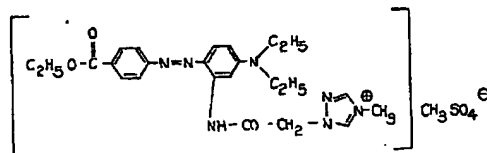
With further diazo components, this coupling component analogously gives the following dyestuffs:



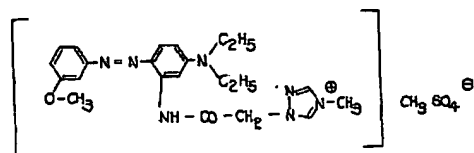
bluish-tinged red



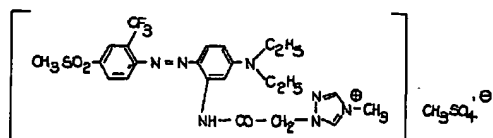
claret red



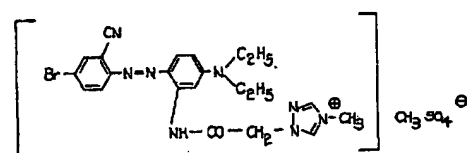
orange



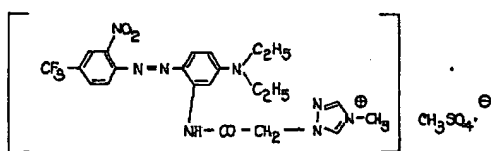
orange



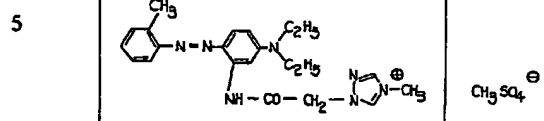
red



bluish-tinged red

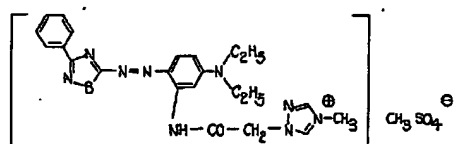


red

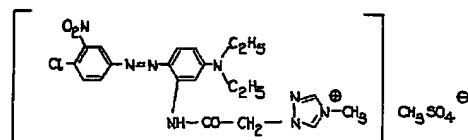


orange

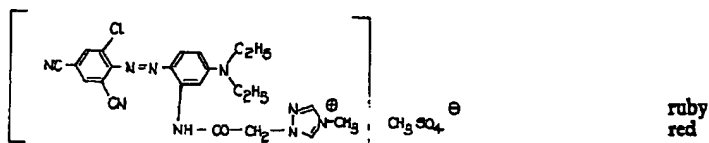
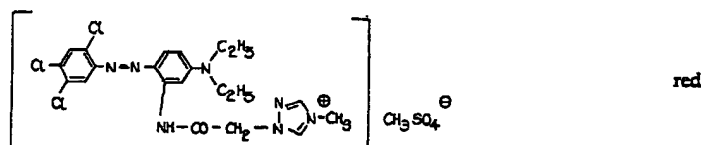
5



reddish-tinged blue



red



#### Example 11.

*Dyeing Process* for polyacrylonitrile and acid-modified polyamide fibres (type Dye I):

0.1 part of the initial dyestuff manufactured according to Example 1 is worked into a paste with approx. 2 parts of water, if appropriate with the addition of a little acetic acid, and dissolved in 50 parts of hot water. Additionally, 0.5—2 g of Avolan IS (condensation product of naphthalene-sulphonic acid and formaldehyde) are introduced into the dyeing liquor, which is made up to 500 parts with cold water. The pH-value of the dyeing liquor is adjusted to 4.5—5 with acetic acid or sodium acetate. 10 g of piece goods of polyacrylonitrile fibres or acid-modified polyamide fibres are constantly agitated in this dyeing liquor whilst raising the temperature to 100° over the course of 30 minutes. The material is dyed at the boil for 60 minutes, rinsed with cold water and subsequently dried at 60—70°.

For dyeing acid-modified polyglycol terephthalate fibres (type "Dacron" 64), a carrier, for example 1—3 parts of an aromatic hydroxycarboxylic acid ester or diphenyl, are further added to the dyeing liquor.

#### Example 12.

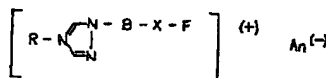
##### Printing Process

A polyacrylonitrile fabric is printed with a printing paste which was manufactured in the following manner: 30 parts by weight of the initial dyestuff of the formula of Example 1, 50 parts by weight of thiodiethylene glycol, 30 parts by weight of cyclohexanol and 30 parts by weight of 30% strength acetic acid are covered with 330 parts by weight of hot water and the resulting solution is added to 500 parts by weight of crystalline dextrin (gum arabic as a thickener). Finally, 30 parts by weight of zinc nitrate solution are also added. The resulting print is dried, steamed for 30 minutes and subsequently rinsed. A red print having very good fastness properties is obtained.

The words "Versatic" and "Dacron" used herein are trade marks. As used herein "known methods" means methods actually in use in the art or described in the literature.

#### WHAT WE CLAIM IS:—

1. A cationic dyestuff of the general formula

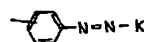


in which

- R denotes an alkyl, alkenyl or aralkyl radical,  
 B denotes a direct bond or a bridge member,  
 X denotes a divalent group,  
 F denotes the radical of an azo-dyestuff and  
 An<sup>(-)</sup> denotes an anion.

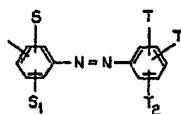
2. A cationic dyestuff according to claim 1 in which B denotes  $-(CH_2)_m-$ ,  $m$  is 0, 1, 2, 3, 4, 5 or 6, R denotes an alkyl group with 1 to 4 carbon atoms or a phenylalkyl group with 1 or 2 carbon atoms in the alkyl chain, X denotes  $-SO_2-$ ,  $-NH-SO_2-$ ,  $-N(alkyl with 1 to 4 carbon atoms)-SO_2-$ ,  $-CO-$ ,  $-NH-CO-$ ,  $-N(alkyl with 1 to 4 carbon atoms)-CO-$ ,  $-O-$ ,  $-S-$ ,  $-NH-$ ,  $-N(alkyl with 1 to 4 carbon atoms)-O-CO-$  or a direct bond, if  $m > 1$ , F denotes the radical of an azo dyestuff,  $An^{m-}$  denotes an anion and wherein the cyclic and acyclic radicals can be substituted by non-ionic radicals.

3. A cationic dyestuff according to claim 2 in which F stands for



in which K denotes the radical of a coupling component of the aniline, phenol, naphthol, naphthylamine, indole, pyrazole, pyridine or pyrimidine series.

4. A cationic dyestuff according to claim 2 in which  $m$  is 0, 1, 2 or 3, and F stands for



in which S denotes a hydrogen atom, a  $C_1$  to  $C_4$ -alkyl radical, a halogen atom or a nitro, methylsulfonyl,  $C_1$  to  $C_4$ -alkoxy,  $C_1$  to  $C_4$ -alkoxycarbonyl radical or a cyano group,

$S_1$  denotes a hydrogen or halogen atom,

$T$  denotes a hydroxyl group or an amino,  $C_1$  to  $C_4$ -dialkylamino,  $C_1$  to  $C_4$ -alkyl-phenylamino,  $C_1$  to  $C_4$ -alkyl-benzylamino, pyrrolidino, morpholino or piperidino radical,

$T_1$  denotes a hydrogen or halogen atom or  $C_1$  to  $C_4$ -alkyl,  $C_1$  to  $C_4$ -alkylcarbonyl-amino or benzoylamino radical and

$T_2$  denotes a hydrogen atom or a  $C_1$  to  $C_4$ -alkoxy radical, or

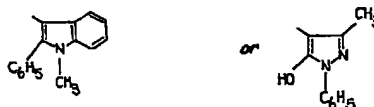
$T_1$  and  $T_2$  together with the phenyl ring denote a naphthyl radical.

5. A cationic dyestuff according to claim 4 in which R denotes a methyl, ethyl or benzyl group, X denotes a  $-SO_2-$ ,  $-NH-SO_2-$ ,  $-N(CH_3)-SO_2-$ ,  $-CO-$ ,  $-NH-CO-$ ,  $-O-$ ,  $-NH-$  or  $-O-CO-$  group, S denotes a hydrogen or chlorine atom, a cyano group or a methyl, trifluoromethyl or methoxy radical,  $S_1$  denotes a hydrogen or chlorine atom,  $T_1$  denotes a hydrogen or chlorine atom or a methyl or acetylamino group,  $T_2$  denotes a hydrogen atom or a methoxy group, T is para to the azo bridge and stands for



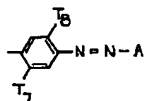
in which  $T_1$  denotes a methyl or ethyl group or an ethyl group substituted by hydroxyl, methoxycarbonyl, chlorine or cyano,  $T_2$  denotes a hydrogen atom or a methyl, ethyl or benzyl group or an ethyl group substituted by hydroxyl, methoxycarbonyl, chlorine or cyano and  $m$  is 1, 2 or 3 and  $An^{m-}$  denotes an anion.

6. A cationic dyestuff according to claim 3 in which R denotes a methyl, ethyl or benzyl group, X denotes a  $-SO_2-$ ,  $-NH-SO_2-$ ,  $-N(CH_3)-SO_2-$ ,  $-CO-$ ,  $-NH-CO-$ ,  $-O-$ ,  $-NH-$  or  $-O-CO-$  group, K denotes a radical of the formulae



m is 1, 2 or 3 and  $An^{m-}$  denotes an anion.

7. A cationic dyestuff according to claim 2 in which F stands for



5 in which A denotes a radical of a diazo component,  $T_7$  denotes a hydrogen or chlorine atom or a  $C_1$  to  $C_4$ -alkyl or alkoxy radical,  $T_8$  denotes a hydrogen or chlorine atom or a methyl, ethyl, acetylamino group or, together with the phenyl ring denotes a naphthyl radical; and in which R denotes a methyl, ethyl or benzyl group, X denotes  $-NH-$  or  $-N(C_1 \text{ to } C_4\text{-alkyl})-$ , m is 1, 2 or 3 and  $An^{m-}$  denotes an anion.

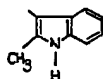
8. A cationic azo dyestuff according to claim 7 in which A stands for



10

15 in which U denotes a hydrogen, chlorine or bromine atom or a trifluoromethyl, cyano, methyl, methoxy, ethoxy, methoxycarbonyl, ethoxycarbonyl, methylsulphonyl or nitro group,  $U_1$  denotes a hydrogen, chlorine or bromine atom or a cyano, nitro, formyl, methylsulphonyl,  $C_1$  to  $C_4$ -alkyl,  $C_1$  to  $C_4$ -alkoxy,  $C_1$  to  $C_4$ -alkoxycarbonyl, phenoxy,  $C_1$  to  $C_4$ -mono- or dialkylaminocarbonyl,  $C_1$  to  $C_4$ -mono or dialkylamino-sulphonyl or phenylazo group, and  $U_2$  denotes a hydrogen, chlorine or bromine atom or a trifluoromethyl, cyano, nitro, methyl, hydroxyl, methoxy, ethoxy, methoxycarbonyl or ethoxycarbonyl group.

9. A cationic dyestuff according to claim 3 in which K stands for

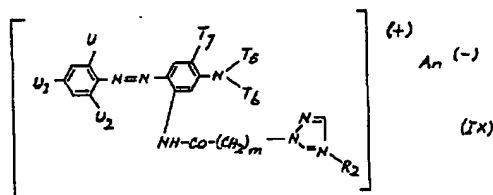


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and R and X have the same meaning as in claim 6.

10. A cationic dyestuff according to claim 1 of the general formula

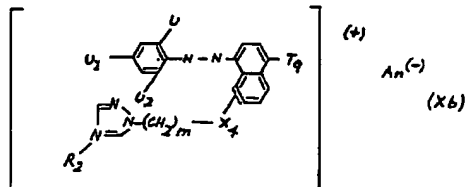


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25 in which  $T_7$ ,  $T_8$ , m and  $An^{m-}$  have the same meaning as in claim 5,  $T_7$  has the same meaning as in claim 7, U,  $U_1$ , and  $U_2$  have the same meaning as in claim 8 and  $R_2$  denotes a methyl, ethyl or benzyl group.

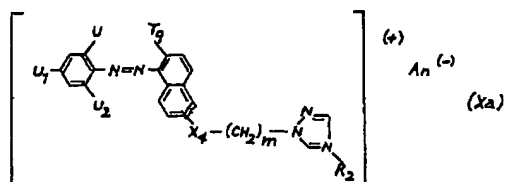
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11. A cationic dyestuff as claimed in claim 1 of the general formula



in which  $m$  and  $\text{An}^{(-)}$  have the same meaning as in claim 5,  $\text{U}$ ,  $\text{U}_1$  and  $\text{U}_2$  have the same meaning as in claim 8,  $\text{R}_2$  has the same meaning as in claim 10,  $\text{T}_q$  denotes  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{NH}(\text{C}_1 \text{ to } \text{C}_4\text{-alkyl})$ ,  $-\text{NH}-\text{C}_6\text{H}_5$ ,  $-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_5$  or  $-\text{N}(\text{C}_1 \text{ to } \text{C}_4\text{-alkyl})_2$  and  $\text{X}_4$  denotes  $-\text{CO}-$ ,  $-\text{CO}-\text{O}-$ ,  $-\text{SO}_2-\text{NH}-$  or  $-\text{SO}_2-\text{N}(\text{C}_1 \text{ to } \text{C}_4\text{-alkyl})-$ .

12. A cationic dyestuff as claimed in claim 1 of the general formula



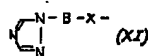
in which  $\text{U}_1$ ,  $\text{U}_2$ ,  $\text{U}$ ,  $\text{T}_q$ ,  $\text{X}_4$ ,  $m$ ,  $\text{R}_2$  and  $\text{An}^{(-)}$  have the same meaning as in claim 11.

13. A cationic dyestuff according to any of claims 2 to 4 in which any of the cyclic and acyclic radicals are substituted by any of the non-ionic substituents hereinbefore specifically mentioned.

14. A cationic dyestuff according to any of the foregoing claims in which  $\text{An}^{(-)}$  is any of those anions hereinbefore specifically mentioned.

15. A cationic dyestuff according to claim 1 as hereinbefore specifically identified.

16. A process for the manufacture of a cationic dyestuff as claimed in claim 1 in which a grouping of the general formula

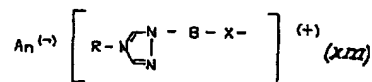


is introduced by known methods into an azo dyestuff or into an amine or azo coupling component, which is diazotised and coupled with a coupling component or coupled with a diazotised amine respectively, and the resulting dyestuff is subsequently quaternised with a compound of the general formula



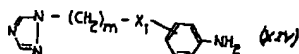
in which  $\text{An}_1$  represents a radical which can be split off under the reaction conditions as an anion and which is identical with  $\text{An}$  or is replaceable by  $\text{An}$ .

17. A process for the manufacture of a cationic dyestuff as claimed in claim 1 in which a grouping of the general formula



is introduced by known methods into azo dyestuff or into an amine or azo coupling component, which is diazotised and coupled with a coupling component or coupled with a diazotised amine respectively.

- 5 18. A process for the manufacture of a cationic dyestuff as claimed in claim 3 in which an amine of the general formula



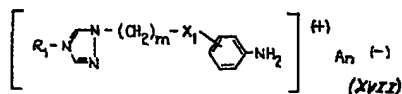
is diazotised and the product is coupled with a compound of the general formula



(XV)

- 10 and is subsequently quarternised with a compound of the general formula (XII) as defined in claim 16.

19. A process for the manufacture of a cationic dyestuff as claimed in claim 1 in which an amine of the general formula

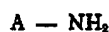


- 15 in which  $\text{R}_1$  and  $\text{X}_1$  have the same meaning as  $\text{R}$  and  $\text{X}$ , respectively, in claim 2, is diazotised and coupled with a coupling component of general formula (XV).

20. A process according to claim 18 in which the amine of general formula (XIV) is any of those hereinbefore specifically mentioned.

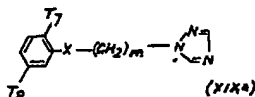
21. A process according to any of claims 18 to 20 in which the coupling component of general formula (XV) is any of those hereinbefore specifically mentioned.

- 20 22. A process for the manufacture of a cationic dyestuff as claimed in claim 7 in which an amine of the general formula



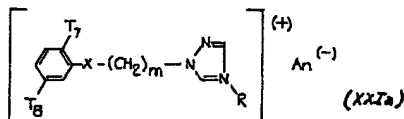
(XVIII)

is diazotised, and the product is coupled with a compound of the general formula



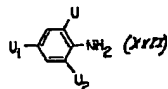
- 25 and is quarternised with a compound of the general formula (XII).

23. A process for the manufacture of a cationic dyestuff as claimed in claim 7 in which the diazotised amines (XVIII), is coupled with a compound of the general formula

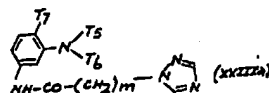


- 30 24. A process according to claim 20 in which the coupling component of the general formula (XIXa) is any of those hereinbefore specifically mentioned as components (XIX).

25 A process for the manufacture of a cationic dyestuff as claimed in claim 10 in which an amine of the general formula

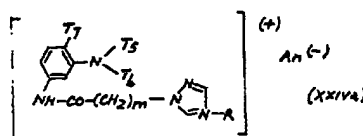


is diazotised and the product is coupled with a compound of the general formula



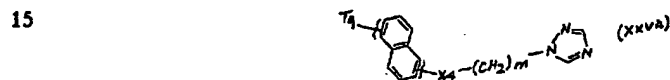
and is quaternised with a compound of the general formula (XII).

- 5 26. A process for the manufacture of a cationic dyestuff as claimed in claim 10 in which the diazotised amine (XXII) as described in claim 25, is coupled with a compound of the general formula



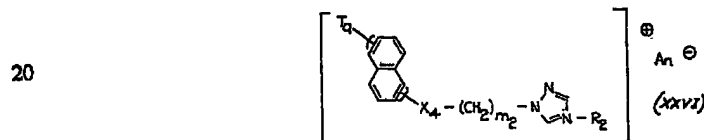
- 10 27. A process according to claim 25 in which the coupling component of the general formula (XXIIIa) is any of those hereinbefore specifically mentioned as components (XXIII).

28. A process for the production of a dyestuff as claimed in claim 11 or 12 in which an amine of general formula (XXII) as described in claim 25 is diazotised and the product coupled with a compound of the general formula



and is quaternised with a compound of the general formula (XII).

29. A process for the production of a dyestuff as claimed in claim 11 or 12 in which an amine of general formula (XXII) as described in claim 25 is coupled after diazotisation, with a compound of the general formula



30. A process according to claim 28 in which the compound of the general formula (XXVa) is any of those hereinbefore specifically mentioned as components (XXV).

- 25 31. A process according to any of claims 22 to 30 in which the diazo components (XVIII) or (XXII) is any of those hereinbefore specifically mentioned.

32. A process for the production of a dyestuff as claimed in claim 1 when carried out substantially as described in any of Examples 1 to 10.

- 30 33. A cationic dyestuff when produced by the process of any of claims 16 to 32.

34. A process for dyeing, printing or bulk dyeing a material which consists wholly or predominantly of a polymerised unsaturated nitrile, of an acid-modified polyester or of an acid-modified polyamide comprising treating the material with a dyestuff as claimed in any of claims 1 to 8, 10 to 15 and 33.



35. A process according to claim 34 in which the unsaturated nitrile is acrylonitrile or vinylidene cyanide.
- 5 36. A process for dyeing or printing a material of tannin-treated cellulose materials, silk or leather comprising treating the material with a dyestuff as claimed in any of claims 1 to 8, 10 to 15 and 33. 5
37. A process for colouring writing fluids, rubber-stamp inks, ball pen pastes or flexographic printing pastes comprising incorporating therein a dyestuff as claimed in any of claims 1 to 8, 10 to 15 and 33.
- 10 38. A process according to claim 33 when carried out substantially as herein-before described. 10
39. A process according to any of claims 34 to 37 in which a dyestuff as claimed in claim 9 is used.
40. A material as defined in any of claims 34 to 37 when dyed, printed, bulk dyed or coloured by the process of any of claims 34 to 38.
- 15 41. A material as defined in any of claims 34 to 37 when dyed, printed, bulk dyed or coloured by the process of claim 39. 15

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